X-ray Scattering Studies of CDW modulated structures in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$

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Declaration

This thesis has been composed by myself and it has not been submitted in any previous application for a degree. The work reported within was executed by me, unless otherwise stated. Some of results of this thesis have appeared in:


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Abstract

The correlation between charge-density waves (CDWs) and superconductivity has been a subject of extensive study for a long time. This thesis describes a series of x-ray scattering experiments designed to study CDWs in perovskite superconductors. A review of the properties of CDW materials and the relationship between CDWs and superconductivity is given. Using x-ray scattering techniques the modulated structures caused by the formation of a CDW state have been clarified in a variety of single crystals of Ba$_{1-x}$K$_x$BiO$_3$. In low resolution measurements, the CDW satellites produce a superstructure doubling of the unit cell existing in the range from the semiconducting state (0<x<0.37) to the metallic state (x>0.37), and which even persists in the low temperature superconducting state. Additional peaks with $G_2=0.33a^*$ were observed in semiconducting samples.

A detailed study of the modulated structure was undertaken using higher resolution x-ray scattering in the metal or superconducting Ba$_{0.6}$K$_{0.4}$BiO$_3$. In this study, the modulated structure was identified to be incommensurate with the host lattice with $G_1=0.494a^*\pm0.011b^*$ and a rather short correlation length of $\sim150\AA$ limited by the CDW domain size. An unusual decrease in the intensities of the CDW superlattice reflections was also observed as the temperature was
lowered.

Evidence to support the attribution of the these satellites to a CDW distortion was obtained from measurements conducted under applied magnetic fields. Increased splitting of the CDW satellites was observed under a magnetic field of 0.8 T with an extremely long relaxation time when the field was removed. Such a long relaxation time is a characteristic of CDWs associated with metastable states. The intensity of the CDW satellites and their peak width remained unchanged up to 0.45 T, but there occurred a remarkable drop in the intensity and a significant decrease in the longitudinal correlation length, while the transverse length remained unchanged, up to 0.8 T. The significance of the CDW distortion in superconducting perovskite oxides is discussed.
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Chapter 1

Introduction

1.1 Introduction

The characterization of the structures of materials is an essential prerequisite for understanding their properties. Various techniques for characterization have been invented to investigate the dynamic and static structure of materials, among which x-ray scattering has the merit of being of general utility.

Recently, owing to advancements in x-ray optics and the availability of intense x-ray sources, such as high brilliance rotating anode generators and synchrotron radiation sources, scientists have been able to further study phenomena when the Bragg condition is nearly satisfied, which means that the contributions due to diffuse scattering and Bragg scattering may be separated in the region of a reciprocal lattice point[1]. The structure of surfaces and buried interfaces can also be studied by the technique of x-ray reflectivity in which the incident x-ray beam falls on the sample at a grazing angle[12][11][6].

With successive crystal reflections, the experimental resolution can be as high
as $10^{-4}\text{Å}^{-1}$ which can be used to study diffraction from near perfect crystals. It should be noted that most of the experimental observations of x-ray diffraction can be explained quite successfully by the kinematical theory as modified by Darwin[3], but currently growing utilization of large perfect single crystals has led to a resurgence of interest in dynamical theory which is more general than the kinematical one, and better suited for analysis of diffraction from highly perfect crystals.

The advantages of a triple-crystal diffractometer are not only shown in the study of layered materials, but also in the search of modulated structures in materials. The occurrence of complex phenomena of materials can result from a distortion in the structure, which is often accompanied by the appearance of a superstructure. Given the very good resolution in two dimensions in the scattering plane, the triple-crystal diffractometer can map out the intensity distribution of scattered x-rays around a reciprocal-lattice point, and therefore it is a powerful tool for searching for weak superlattice reflections.

Since the discovery of the high-$T_c$ superconductors, the role played by the modulated structure in high-$T_c$ superconductors has been under intense scrutiny, in the hope of revealing clues about the mechanism of high-$T_c$ superconductivity. Superstructures have been observed in many high-$T_c$ cuprates by electron diffraction, x-ray and neutron diffraction in numerous works [15], but the interpretation is somewhat difficult due mainly to the complex structures. However the synthesis of the copper-free high-$T_c$ superconductor $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ has opened a new way toward the understanding of high-$T_c$ superconductivity. The parent compound $\text{BaBiO}_3$ has a monoclinic structure and is an insulator despite the
metallic prediction of the band structure calculation. Owing to the different Bi-O bond lengths, a model involving charge-density wave (CDW) was proposed to explain the insulating nature. A key question that the remainder of this thesis addresses is the extension of the CDW superstructure model from BaBiO$_3$ into Ba$_{1-x}$K$_x$BiO$_3$. This thesis therefore uses results from x-ray scattering experiments on crystals of Ba$_{1-x}$K$_x$BiO$_3$ to study the occurrence of CDW modulated structures into the perovskite superconductor superconductor Ba$_{0.6}$K$_{0.4}$BiO$_3$. 
Chapter 2

Charge-Density Waves

2.1 Introduction

The electronic state of a crystalline material with a partially filled band, in which the electronic degrees of freedom are characterized by the Fermi surface, may not be metallic but insulating so as to minimize the energy gained when the temperature is lowered. Such an anomalous behaviour always accompanies the presence of additional periodicities induced either by virtue of a lattice distortion or density waves in the electron system. In such cases the Fermi surface and, hence, the electronic energy is modified. This instability resulting from the presence of a periodic lattice distortion was first proposed by Peierls and is called a Peierls instability [17]. Depending on the nature of the distortion, there are various instabilities occurring at the Peierls transition temperature, $T_p$, such as the spin-Peierls state in the spin-1/2 antiferromagnetic low-dimensional compounds [18] [196], the spin-density waves (SDW) [20], and the charge-density waves (CDW) [21]. The later two are due mainly to the redistribution of charge densities, and
the ground state of spin-density waves is a consequence of electron-electron interactions which give rise to a local magnetic moment, but electron-phonon interactions are responsible for the presence of a charge-density wave state which has no local magnetic moment. However, accompanying these instabilities is the opening of a gap at the Fermi surface which drives the materials to a metal-semimetal or metal-semiconductor transition at the transition temperature.

2.2 Peierls Distortions

It was suggested more than thirty years ago by R. E. Peierls [17] that a one-dimensional metal is unstable toward the formation of a periodic lattice distortion at low temperature when the electron system of one-dimensional metal couples to the underlying lattice. The ground state of the coupled electron-phonon system is characterised by a gap in the single-particle excitation spectrum and by a collective mode formed by electron-hole pairs involving the wave vector $q=2k_F$.

In a general case without considering the existence of the Peierls distortion, the interaction of the electrons with the underlying ions transforms the free electron spectrum into Bloch states, leading to gaps at the Brillouin zone edge. Some of these structures may be visualized by starting from a very simple lattice and introducing a slight displacement of the atoms. If all the atoms are equally spaced in a line with a periodic repeat distance $a$, then all multiples of $a$ are lattice vectors, and the energy curve $E(k)$ for an electron in the potential of the original chain is as displayed in figure 2-1.

Now suppose the chain has been distorted by displacing atoms a little, the displacement repeating every 3rd atom. This immediately reduces the translational
symmetry and only multiples of $3a$ are lattice vectors. The cell in reciprocal space is now

$$\frac{-\pi}{3a} < k < \frac{\pi}{3a}.$$  

This periodic potential couples states at $+k_f$ and $-k_f$, $k_f=\pi/3a$, which have the same energy. Such degenerate states are split by the potential to form one state with a higher energy than the original states, and one state with lower energy; and the result is a gap ($\Delta$) opened at the Fermi energy, where $\Delta$ is proportional to the amplitude of the distortion; the total electronic energy is therefore lowered. The modified energy spectrum looks as shown in figure 2-2. Therefore the opening of a gap at the Fermi surface is responsible for the occurrence of a semiconducting state below the Peierls transition temperature $T_P$.  

**Figure 2.1.** Schematic representation of the energy band of an undistorted atomic chain.
Figure 2.2. Energy band structure of a Peierls distortion of an atomic chain.

2.3 Charge Density Wave State

As given above, in a one-dimensional metal with a partly filled band the lattice will never be stable because the presence of the periodic potential will break the Fermi surface distribution. If the periodic potential comes from an electron-phonon interaction, then the result is a one-dimensional semiconducting state accompanied by a lattice distortion and the formation of a charge-density wave (CDW) which is a sinusoidal modulation of the charge density along the chain [25]. This instability also possesses the common nature of the Peierls distortion, i.e. characterised by the opening of a gap at the Fermi surface and by a softening in the phonon spectrum at the $Q=2k_f$ where $k_f$ is the Fermi wave vector [22].

In a one-dimensional metal at $T=0$ the corresponding ground state without
Figure 2.3. The free electron density and energy distribution of free electron states of an undistorted atomic chain.

The presence of distortions is shown in figure 2-3. The electron states are filled up to the Fermi level $\epsilon_F$, and the lattice is a periodic array of atoms with lattice constant $a$. Consider the case of an uniform chain of atoms with spacing $a$ and a periodic structural distortion. Sequentially, the rearrangement of ions in the metal is accompanied by a corresponding spatial modulation of the concentration of its conduction electrons whose redistribution tends to restore electrical neutrality. Now the charge density in the crystal is given by

$$\rho(\mathbf{r}) = \bar{\rho} + P \cos(Qr + \phi).$$

Where $\bar{\rho}$ is the average electronic density, $P$ is the amplitude of the electronic density wave, $Q = 2k_f$ is the CDW wave vector, and $\phi$ is the CDW phase with
respect to the undistorted lattice. The ground state exhibits a periodic modulation of the charge density and a lattice distortion, namely a charge-density wave (CDW), and the single particle excitations have a gap, $\Delta$, related to the amplitude $P$ at the Fermi level. In such a case the electron density on each ion is sinusoidally modulated as shown in figure 2-4.

![Diagram](image)

**Figure 2.4.** A charge-density wave in a one-dimensional metal. The graph shows the sinusoidally modulated density of conduction electrons and the corresponding energy band.

The above discussion of the charge-density wave state has been at temperature $T=0$. At finite temperatures normal electrons excited across the single-particle gap screen the electron-phonon interaction. This in turn leads to the reduction of the gap and eventually to a second-order transition at the Peierls temperature $T_P$. The material is a metal above the transition temperature while it is a semiconductor below $T_P$ with a temperature-dependent gap $\Delta(T)$. 
Chapter 2: Charge-Density Waves

When the charge-density wave modulation is commensurate, the distortion of charge and atomic displacement simply gives the crystal a larger unit cell. For instance, if the modulated wavevector is equal to one third of the reciprocal lattice vector $a^*$, then the distorted unit cell is three times the undistorted unit cell and the crystal structure is still periodic. When the modulation is incommensurate with the host lattice then the distorted unit cell can not contain an exact period of both the density wave and the underlying crystal structure. The material is no longer periodic; the whole sample is the unit cell. The energy of a CDW (in an ideal crystal) would be independent of its phase and the energy of the system would be independent of their relative positions, and thus no potential barrier opposes the motion. In real systems, as shown by Lee, Rice, and Anderson [23], the gapless character of the phase mode is destroyed through various mechanisms, especially impurity pinning.

The dynamics of sliding charge-density waves are dominated by both the phase and amplitude coordinates of the CDW order parameter. The dispersion relation for the amplitude mode is gapped so that a finite amount of energy is required to create amplitude excitations. In contrast, the dispersion relation for the phase mode of incommensurate CDW's is linear [65]. Both low-energy excitations of the CDW ground state give rise to two branches called, respectively, amplitudon and phason in the phonon spectrum below $T_p$. A very small amount of energy, such as the interaction between the imperfections in crystal and the CDW's, is enough to generate phase excitations in perfect crystals. In spite of the defect pinning this introduces a gap into the energy spectrum, but for weak pinning, phase excitons remain easier to excite than amplitude excitations [24][56]. Consequently, most models devoted to discussing CDW transport phenomena have focused on the
dynamics of the CDW phase mode.

Both the phase and amplitude mode dispersion relations can be examined using inelastic neutron scattering or optical experiments. Phase excitations result in the displacement of the electronic charge density, and consequently the phase is optically active. No charge fluctuation occurs for amplitude fluctuations, therefore the amplitude mode is Raman active [65][37]. Using inelastic neutron scattering Sato et al. [40], Lynn et al. [41] and Hennion [42] have revealed the existence of temperature-dependent excitations that have been interpreted as phase and amplitude modes in CDW materials K$_{0.3}$MoO$_3$ and K$_2$[Pt(CN)$_4$]Br$_{0.3}$·zH$_2$O (KCP).

For an incommensurate CDW, such as develops in NbSe$_3$ in both charge-density wave states, the phase can be arbitrary with respect to the underlying lattice. In this case, the energy of the system is phase independent. With an arbitrary phase, arbitrary small applied electric fields can lead to a current carried by the CDW condensate.

2.4 Observations of CDWs

The materials listed in table 2-1 possessing a CDW modulation have the basic structural units forming chains with strongly overlapping electronic wave functions along the chains and only weak overlap in the perpendicular directions. This leads to a quasi-one-dimensional electronic band structure, the necessary prerequisite for a Peierls transition, and a highly anisotropic conductivity. Niobium triselenide, NbSe$_3$, is the first material which was observed to have the CDW modulation. The compound NbSe$_3$ shows a sharp increase in resistivity measured
Table 2.1. Some conventional CDW materials

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_1$(K)</th>
<th>$q_a$</th>
<th>$q_b$</th>
<th>$q_c$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbSe$_3$</td>
<td>144</td>
<td>0</td>
<td>0.2412</td>
<td>0</td>
<td>[26]</td>
</tr>
<tr>
<td></td>
<td>59</td>
<td>0.5</td>
<td>0.2604</td>
<td>0.5</td>
<td>[27][28]</td>
</tr>
<tr>
<td>O-TaS$_3$</td>
<td>215</td>
<td>0</td>
<td>0.1</td>
<td>0.255</td>
<td>[30]</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>0.5</td>
<td>0.125</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>$2H$-TaSe$_2$</td>
<td>122.3</td>
<td>0.3267</td>
<td>0</td>
<td>0</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>1/3</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$2H$-NbSe$_2$</td>
<td>33.5</td>
<td>0.3252</td>
<td>0</td>
<td>0</td>
<td>[29]</td>
</tr>
<tr>
<td>(TaSe$_4$)$_2$I</td>
<td>263</td>
<td>1</td>
<td>0</td>
<td>0.943</td>
<td>[31]</td>
</tr>
<tr>
<td>K$_{0.3}$MoO$_3$</td>
<td>180</td>
<td>0</td>
<td>0.263</td>
<td>0.5</td>
<td>[195]</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0</td>
<td>0.25</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Rb$_{0.3}$MoO$_3$</td>
<td>180</td>
<td>0</td>
<td>0.26</td>
<td>0.5</td>
<td>[33]</td>
</tr>
</tbody>
</table>

along the chain direction at $T_1$=144 K and $T_2$=59 K, and reaches a maxima at 125 K and 49 K as shown in figure 2-5. Below 49 K it returns to a metallic-type temperature variation of the resistivity. The resistivity anomalies observed in NbSe$_3$ have been associated with the opening of gaps at the Fermi surface as a result of the formation of charge-density waves. The residual conductivity at low temperatures has been ascribed to a partial destruction of the Fermi surface which leaves nondestroyed electron-hole pockets. This has been confirmed by Hall-effect [38] and by magneto-resistance measurements [87].

Other extensively studied CDW materials are K$_{0.3}$MoO$_3$ and Rb$_{0.3}$MoO$_3$. The basic crystallographic structure is built with infinite sheets of MoO$_6$ octahedra separated by K ions. In spite of its layered-type structure, K$_{0.3}$MoO$_3$ shows a high electrical conductivity along the $b$ direction made of infinite chains of MoO$_6$ octahedra, and therefore can be considered as a quasi-one-dimensional metal. The quasi-one-dimensional material K$_{0.3}$MoO$_3$ is well known to be a model representative of a variety of compounds exhibiting the charge-density
Figure 2.5. Temperature dependence of the resistivity of NbSe$_3$. 

\(\rho(10^3 \Omega \text{cm.})\)

\(T_{1}\)

\(T_{2}\)
wave (CDW) ground state at low temperatures. $K_{0.3}MoO_3$ undergoes a metal-semiconductor transition at $T_c \sim 180$ K, indicating that the Fermi surface has been almost destroyed. This gap opened at the Fermi level is accompanied by the appearance of an incommensurate superlattice as detected by x-ray scattering [see table 2-1].

The opening of a gap at the Fermi surface due to the formation of a charge-density wave (CDW) has remarkable influences not only on the transport properties but also on the appearance of Bragg diffraction satellites. In the CDW state the modulation of charge causes each ion to see a different potential. The resulting forces in turn cause each ion to be displaced to a new equilibrium position. The modulation of ionic displacements $u_n$ will have the form [34]

$$u_n = u_0 \sin(nQa + \varphi)$$

where $n$ is an integer defining the position of the ion. The $Q$ and $\varphi$ are the wavevector and the phase of the CDW. The amplitude must be small compared to $a$ if the crystal is not to be disrupted. In an undistorted structure the only allowed scattering vectors for x-rays are the reciprocal lattice vectors $G$. For the case of a simple-cubic lattice these are

$$G_{hkl} = (h\hat{x} + k\hat{y} + l\hat{z})2\pi/a.$$ 

If the structure is distorted by a periodic potential then each ion will be displaced from its equilibrium lattice site. A Fourier analysis of this ion density will now have additional Fourier components giving rise to the new scattering
Chapter 2: Charge-Density Waves

vectors

\[ q = G_{\text{me}} \pm Q. \]

There are, therefore, two CDW satellites associated with each reciprocal lattice; their intensity may be two to eight orders of magnitudes smaller than the intensities of ordinary Bragg reflections [35]. The satellite reflections resulting from periodic modulations in their lattice constants are visible in all diffraction experiments with x-ray, neutrons and electrons.

\textit{NbSe}_3 is known as a linear-chain compound which exhibits a variety of non-linear transport properties associated with two incommensurate charge-density waves (CDW) which are formed independently. Using synchrotron x-ray scattering Fleming and co-workers [26] were able to determine the modulated superstructure of the CDW in NbSe_3. The CDW's form at phase transitions at \( T_1 = 144 \) K and \( T_2 = 59 \) K, and they have reduced wave vectors of \( q_1 = (0.2412 \, 0) \) and \( q_2 = (0.5 \, 0.2604 \, 0.5) \), respectively. It is noteworthy that \( q_1 \) has various behaviours when the temperature is lowered [27]. Upon cooling, the profile of \( q_1 \) along the chain direction \( b^* \) sharpens, indicating a development of long-range order at 80 K [see figure 2-6]. By measurements of the inverse correlation lengths, \( \xi \) along the \( a^*, b^* \) and \( c^* \) directions, the authors obtained the anisotropy ratios of \( \xi_{b^*}/\xi_{a^*} \sim 3.5 \) and \( \xi_{b^*}/\xi_{c^*} \sim 27 \), which reflects two-dimensional CDW fluctuation in the \( (a,b) \) planes at \( T_1 \). Such charge-density wave fluctuations have also been found in other CDW materials such as \textit{K}_0.3\textit{MoO}_3 [148], \textit{TaS}_3 and \textit{(TaSe}_4\textit{)}\textsubscript{2}I [44] and has a pronounced influence on the density of state (DOS) and the formation of the pseudogap which can result in the decrease of the conductivity. Other measurements [45] [46] [47]
Figure 2.6. a: The evolution of line widths of $q_1$ with temperature. b: Temperature variation of the incommensurate wave vector of $q_1$. Data were obtained from synchrotron x-ray scattering on a pure single crystal NbSe$_3$ [27].
also show significant deviations from mean field behaviour and are suggestive of a critical fluctuation region near the transition temperature.

The blue bronze $K_{0.3}MoO_3$ is another extensively studied CDW material due to the availability of large single crystals. $K_{0.3}MoO_3$ undergoes a metal-semiconductor phase transition at $T=181$ K where a charge-density wave state is formed [48]. Utilising both x-ray and neutron scattering measurements Fleming et al. [195] identified the CDW wave vector is incommensurate with the underlying lattice at an onset temperature $T=181$ K with a reduced wave vector of $q=(0 0.263 0.5)$. Upon cooling, an incommensurate-commensurate transition occurs and the CDW vector becomes $q=(0 0.25 0.5)$ at $T=100$ K. Measurements of the dc threshold electric field also display a maximum in the depinning field at about 100 K, very close to the $C$-$I$ transition. However this behaviour is different from what has been found in NbSe$_3$ [49] and TaS$_3$ [50], and may result from a deformation of the internal degrees of freedom of the commensurate CDW condensate or less phase fluctuation effect in a commensurate CDW state than that in an incommensurate CDW state [51].

Measurements of the intensity of CDW peaks can provide the information related to the amplitude of the CDW distortion, while the gap, $\Delta$, opened at the Fermi surface due to the charge density modulation is also proportional to amplitude $P$ of the CDW [52] [65] [148] [55]. Calculation of the intensity of a charge-density wave diffraction gives rise to the formula

$$I(q) \sim \Delta^2.$$  

The temperature dependence of this square of the CDW order parameter can
therefore be deduced from the integrated superlattice peak intensity, which evi-
dences a second order phase occurring in these CDW materials measured as
displayed in figure 2-7. Further studies on these data provide the best fitting
within the framework of the weak coupling BCS theory. However this comes into
conflict with the results coming from the optical measurements and the tunnel-
junction spectra [53] [54]. The single-particle gaps determined directly by both
measurements gives rise to the ratio $2\Delta/k_B T_{CDW}$ being significantly larger than
the mean-field BCS value of $2\Delta/k_B T_{CDW}=3.5$. The ratio is close to 14 at $T=59$
K in NbSe$_3$, and it is interpreted as resulting from the strong-coupling nature
of electron-phonon interactions. This deviation probably comes from the large
anisotropy inducing phase fluctuations and leading to $T_{CDW}$ smaller than the
mean-field transition temperature.

2.5 Impurity effects of CDW

Impurities distributed at random in the crystal have a profound influence on both
the static and dynamic properties of charge-density waves. Many anomalous
phenomena in the transport measurements observed in the CDW materials are
the consequence of the interaction between the collective mode and the lattice
irregularities. This interaction leads to a finite pinning energy, and this in turn
shifts the oscillator strength and also results in a finite dc threshold for nonlinear
conduction. There is a great deal of experimental evidence to suggest that the
impurities play an important role in pinning or depinning the collective mode
behaviour [55]. Theoretically there have been many papers discussing the role
played by impurities in a system in less than 4 dimensions. As first argued by
Figure 2.7. Temperature dependence of the integrated intensity of the CDW superlattice reflection in the CDW materials NbSe$_3$, K$_{0.3}$MoO$_3$ and (TaSe$_4$)$_2$I. The solid line is fitted in the weak coupling BCS limit [65].
Sham and Patton [58], Imry and Ma [59], and Efetov and Larkin [60], impurities positioned at random destroy the long-range order and lead to the phase-phase correlation function being of the form

$$\exp^{i[\varphi(r)-\varphi(0)]} \sim \exp^{-r/L}$$

where the characteristic length scale $L$ depends on the strength of the impurity potential and on the elastic properties of the condensate. This macroscopic length scale, namely the Fukuyama-Lee-Rice domain length $L_{FLR}$, characterizes the decay of phase correlations in the pinned CDW's state due to the interaction of the CDW with randomly positioned impurities. As the phase is completely adjusted to the impurity positions at every impurity site, in the strong pinning region, the average phase-phase coherence length [56],

$$L_{FLR}^S \sim n_i^{-1}$$

is the average distance between impurities. On the other hand, in the weakly pinning case, minimizing the total energy originating from the impurity potential and the elastic energy of CDW's with respect to the domain size, this characteristic length can be deduced as [191] [70][65]

$$L_{FLR}^W \sim V^{2/d-4} n_i^{1/d-4}$$

where $V$ is the impurity potential associated with the impurities concentration $n_i$, and $d$ the dimensionality of the CDW. This finite static phase coherence length
Chapter 2: Charge-Density Waves

contributes to the nature of a static CDW, and is roughly the length over which the phase fluctuations are less than $2\pi$. The characteristic lengths discussed above are obtained without consideration of the thermal fluctuations in the phase of the CDW. For most CDW conductors, $L_{FLR}$ is estimated to be on the order of one micron (1000 Å) or less because of the presence of impurities. The application of electric fields drives the dynamic phase-phase correlation length to form a microscopic domain volume [68]. Within this domain the phase of the CDW can be regarded as a rigid entity, as the sample volume increases, different microscopic domains oscillate out of phase and result in the size effect in the narrow-band noise response [69].

The problem of many impurities distributed at random can be treated within the framework of the Ginzburg-Landau description, in which potentials induced by impurities couple directly to the phase of the charge-density condensate and lead to a finite phase-phase correlation length. This length scale depends on the strength of the impurity potentials and on the impurity concentration. The absence of long range order, and the appearance of many metastable states have been also ascribed to the pinning effect of the impurities.

There are two pinning limits depending on the strength of the defect potential with respect to the deformation energy of the CDW; they are so-called strong impurity pinning and weak impurity pinning as shown in figure 2-8. Both factors involve two competing energies, the elastic energy of the CDW condensate and the impurity energy [56] [191]. If the impurity potential dominates, the phase of the CDW will adjust itself at each impurity site and then the system arrives in the strong pinning case, wherein the phase is pinned at the $j$th impurity site at the value $\Phi_j$ and minimizes the the energy of interaction of the CDW with the
Figure 2.8. The spatial phase distortions in the presence of impurities. a: the original CDW, b: the strong pinning adjusts the phase at each impurity site, c: for weak pinning such phase adjustment occurs over a characteristic distance $L$. 
\$j\$th impurity; it can be considered as an individual mechanism of pinning. When many strong-pinning centres are present, the CDW phase would be smoothly interpolated on adjacent sites over a length scale proportional to \(n_i^{-1}\). In this case the transport response is that of the sum of the individuals regarded as a charged oscillator. The depinning field in this regime depends linearly on the concentration of impurities [191],

\[
E_T^s \sim n_i
\]

which has been verified in some experiments [64].

Oppositely, is the system of the so-called weak pinning, and the characteristic pinning energy can be orders of magnitude smaller than the relevant single particle energies such as the band gap or bandwidth. In contrast to what happens for strong impurity potentials, the phase is pinned to randomly distributed impurities with a length significantly exceeding the average distance between impurities. The competition resulting from the elastic energy and the impurity potential results in the depinning energy being proportional to the square of the impurity concentration [191] [65] [66] [63],

\[
E_T^w \sim n_i^2
\]

In the weak pinning limit the individual impurity is unable to pin the phase of CDW condensate to any preferred value, but these weak impurities can still pin the overall phase of the CDW [56] [58]. In such a state, the phase varies
slowly from the one impurity site to the next, indicating that the phase varies on a scale much greater than the impurity spacing $n_i^{1/(d-4)}$, where $n_i$ is the impurity concentration and $d$ is the dimensionality of the CDW.

The Fukuyama-Lee-Rice (FLR) model [56][191] not only provided a good interpretation of experimental findings [71][63][72] of the dependence of the threshold field $E_T$ and the impurity concentration $n_i$ as $E_T \sim n_i$ and $E_T \sim n_i^2$, but also predicted a divergence of $E_T$ as the temperature $T$ approaches the transition temperature $T_c$. On the other hand, at lower temperature (e.g., $T < 1/2 T_c$), the FLR theory predicted that $E_T(T)$ was independent of temperature. However, in a number of measurements the threshold field $E_T(T)$ was shown to depend on $T$. Extending the FLR theory to finite temperatures and including the thermal fluctuation of the phase of the CDW order parameter, K. Maki [51] demonstrated that the temperature dependence of the threshold field at low temperatures is given by

$$E_T(T)/E_T(0) = \exp^{-\left(T/T_0\right)}$$

while the FLR length $L_{FLR}(T)$ is rescaled as

$$L_{FLR}(T)/L_{FLR}(0) = \exp^{T/2T_0}$$

where $T_0$ is a material constant [67]. Such a rescaled model was shown to be in agreement with the experimental data [73].

Without considering the impurity effect, the ordered phase in the Peierls distortion system would give rise to a long-range-ordered superstructure, but in a
real system impurities always destroy this ordered state and lead to a short range order [58] [59]. Such a behaviour has been observed by Moncton and co-workers using neutron diffraction on the CDW system 1T-Ta$_{1-x}$Zr$_x$Se$_2$ with varying impurity (i.e., Zr) concentration [61]. In the clean limit (x~0) the CDW superlattice possesses a long-range order with a correlation length (perpendicular to the layer direction) longer than $\varepsilon \sim 500$ Å. The addition of Zr impurities (x~0.03) reduces markedly the length to $\sim 13$ Å. Similar effect was also observed in the vanadium-doped blue bronze K$_{0.3}$V$_x$Mo$_{1-x}$O$_3$ [62].

More direct experimental evidence for finite correlation lengths influenced by impurities has been provided by the study of the profile of the CDW superlattice satellites using high resolution x-ray scattering in which impurities are introduced by alloying or irradiation.

The absence of long-range order has several important effects on the static and dynamic properties of density waves and leads to a broadening of the x-ray reflections of the CDW superstructure, and the satellite peak profiles corresponding to the CDW wavevector $\vec{Q}$ can be fitted as

$$I(\vec{k}) \sim \frac{\Gamma}{(\vec{k} - \vec{Q})^2 + \Gamma^2}.$$ 

The half-width $\Gamma = 1/\xi$, and this therefore gives the phase-phase correlation length $\xi$ directly. Experimentally, the phase coherence lengths in doped or irradiated CDW materials have been studied using x-ray scattering, but only on few cases [75] [62] [74] [28]. The common feature in these studies is the decrease of the correlation length of CDW satellite reflections with increasing impurity
or defect concentration. By studying the structure of charge-density wave $Q_1$ in pure and Ta-doped NbSe$_3$ Dicarlo and co-workers interpreted the relationship between the decreased length and the impurity concentration within the weak-pinning model of Fukuyama-Lee-Rice [56] [191]. However, in a systematic investigation on electron-irradiated blue bronze (K$_{0.3}$MoO$_3$) by DeLand et al. [74], the measured width of the CDW satellite peaks is found to have a concentration dependence of $n_i^{-0.4}$ in clear contrast to the consequences of weak impurity pinning which predicts that $L_{FRL}^W$ is inversely proportional to the impurity concentration, i.e. $L_{FRL}^W \sim 1/n_i$, as shown in figure 2-9.
Figure 2.9. The relationship of CDW satellite peak widths and of nearby Bragg peak widths with impurity concentration in K$_{0.3}$MoO$_3$ [74].
Chapter 3

Charge-Density Waves and
Superconductivity

3.1 Introduction

Prior to BCS theory being developed to explain superconductivity, Frohlich, [83] proposed another mechanism for superconductivity based on the electron-phonon interaction, in which a one-dimensional metal develops a charge density wave (CDW) state with an additional periodicity through the electron-phonon interaction. This modulation is accompanied by a lattice distortion of the form $u(r)=u_1 \cos[Q \cdot r + \phi(r, t)]$, where $|Q|=2k_F$ is the CDW wave vector and $\phi$ is the phase of the CDW order parameter. In a perfect crystal, an incommensurate CDW would have no preferred phase $\phi$, and the CDW then could slide freely through the crystal, resulting in collective charge transport and a current $I \propto d\phi/dt$. However there are various mechanisms that can pin the CDW in real crystals, and thus at finite temperatures the system can fluctuate into
Chapter 3: Charge-Density Waves and Superconductivity

the current-carrying excited state which might give an unusually high resistivity, i.e. a semiconducting state. Although pinning can destroy the current carriers formed, in the incommensurate charge-density wave state there is still the possibility of a superconducting state at low temperatures.

In a superconducting state current carriers are no longer individual electrons as in the normal metallic state, but pairs of electrons, Cooper pairs, having opposite momenta (i.e., opposite wave-vectors). In 1957, J. Bardeen, L. N. Cooper and J. R. Schrieffer constructed the BCS theory to explain the superconductivity observed in conventional superconductors [86]. They considered two electrons added into a non-interacting Fermi gas at 0 K where all the states are filled for $k < k_\text{F}$ and both electrons occupy states with $k > k_\text{F}$ because of the Pauli-exclusion principle. There will be a net attractive electron-electron interaction when the first electron moves through the crystal to cause a lattice distortion in such a way that a second electron reduces its energy by moving through the distorted structure. For electrons moving in such a correlated fashion, it was suggested that the interaction is attractive, and larger, than the repulsive, screened-Coulomb interaction between electrons, this is called phonon-mediated pairing. Interactions between the electron pairs introduce an energy gap at the Fermi surface, and this gap prevents Cooper pairs from breaking up when there is no excitation energy greater than the gap. Thus the electron-electron attraction mediated by the electron-phonon coupling is essential for the occurrence of superconductivity. The superconductivity observed in most of conventional superconductors can be explained well within this BCS-superconducting model. Following the discovery of some new superconducting materials, like the heavy fermion superconductors and the high-$T_c$ cuprates, the ordinary BCS theory is no longer sufficient.
Instead, various models have been proposed to explain the unconventional superconductivity. Although much effort has been made to achieve high transition temperatures, the origin of this unconventional superconductivity is still an area of continuing research.

3.2 Sliding CDWs

Materials having a charge-density wave distortion are inherently nonlinear systems, as the applied electric field exceeds the threshold value $E_T$. There are a great number of experiments demonstrating that the nonlinear conductivity observed in the charge-density wave state is a new collective transport phenomenon, and highly suggestive that the current is carried by the sliding CDW through mechanisms proposed originally by Frohlich [83] [23]. As a model of the Peierls transition Frohlich considered the coupling of noninteracting electrons and phonons in a system, and showed that the distorted phase can carry a current by propagating the combined lattice and electronic charge distortion as a travelling wave. Since an energy gap has been introduced in the electronic spectrum, Frohlich argued that this wave will propagate freely and the conductivity will be infinite. This result can be understood as a consequence of a non-pinning charge-density wave. However this charge-density wave (CDW) is always pinned by imperfections in the crystal, so it needs additional energy to overcome the pinning potential produced by the imperfection. Thus a non-linear transport behaviour is expected due to the pinning effect.

A typical example of anomalous electron transport properties caused by a
Chapter 3: Charge-Density Waves and Superconductivity

charge-density wave distortion is the measurement of dc resistivity in the transition-metal trichalcogenide NbSe$_3$ as shown in figure 3-1. Niobium triselenide NbSe$_3$ is a quasi-one-dimensional metal with a high conductivity along the chains of Nb atoms that run parallel to the $b^*$ axis. The dc resistivity shows two peaks in the vicinity of 125 and 49 K. These points are associated with the occurrence of two independent incommensurate charge-density waves. Above 145 K the conductivity of NbSe$_3$ increases as temperature decreases, showing a metallic behaviour. Upon further cooling, at $T_1=145$ K and $T_2=59$ K the resistivity increases sharply and reaches maxima at 125 K and 49 K. The increase in the resistivity is ascribed to the gaps opened at the Fermi surface due to the formation of two CDWs at $T_1$ and $T_2$, respectively. The application of current densities exceeding a certain value causes both peaks to be suppressed. However, the suppression of the lower peak is more dramatic. A 50% reduction of the lower temperature feature requires only $\sim 3$ Amm$^{-2}$ compared to $\sim 90$ Amm$^{-2}$ for the higher peak. The band-structure calculation [175] shows that the Fermi surface is composed of nearly planar sheets oriented perpendicular to the $b$ axis, these provide the nesting conditions which drive the CDW transition. This suggests that the CDW transition at $T_1$ arises from the Fermi surface sheets that produce nearly perfect nesting while the transition at $T_2$ arises from only partially nested sheets. These transitions result in a substantial reduction of the Fermi surface area, but the remaining normal Fermi surface sections provide for semimetallic conductivity down to the lowest temperatures. It has been found that the application of pressure results in a decrease in the critical temperature for the CDW formation (this will be discussed more fully in the next section), which was interpreted as due to a shift in the Fermi surface caused by applying pressure which increases the strain.
Figure 3.1. Nonlinear resistivity of NbSe$_3$ as a function of temperature at various current densities (A/mm$^{-2}$) [95].
energy. In contrast, the decrease in the resistivity by applying an electric current results from a different mechanism; it does not affect the transition temperatures $T_1$ and $T_2$. Based on the framework of the impurity pinning model of the CDW condensate, the significant enhancement of the conductivity by applying electric fields exceeding the threshold value arises from the depinning of the rigid CDW condensate which is then accelerated by the electric field. However, the depinning field has been believed to be sensitive to an incommensurate-commensurate lock-in transition. In orthorhombic-TaS$_3$ the threshold electric field has a maximum around 14 K where the lock-in transition occurs [88].

The impurity pinning effects also give rise to a temperature dependence of the threshold electric field, $E_T$ [56] [191] [73]. Measurements show that the electric field required to overcome the pinning potential produced by impurities positioned at random increases as the temperature decreases below both transition temperatures. This temperature dependence of $E_T$ can be attributed to the increase in the screening length associated with the reduction in the normal electron density at lower temperatures. That is, at low temperatures the screening becomes less effective, and thus the CDW is more strongly pinned, and hence $E_T$ increases. It is also noticeable that the field strength for depinning the CDW is divergent upon approaching both transition temperatures from below $T_1$ and $T_2$, respectively. This observed divergence of the depinning field can be explained within the model proposed by Fukuyama, Lee and Rice FLR [191]. They demonstrated that the depinning field should diverge as the $\Delta^{-\eta}$ where $\Delta$ is the gap opened by the CDW at the Fermi surface and $0<\eta<1$ as $T$ approaches the transition temperature. Considering the effects of thermal fluctuations in the phase
of the CDW, Maki deduced a modified FLR theory \[^{[51]}\] \[^{[73]}\] which fits the experimental data quite well as shown in the solid lines of figure 3-2.

Field-dependent changes in the CDW structure are also expected as a consequence of impurity pinning. Using synchrotron x-ray scattering DiCarlo et al. \[^{[89]}\] observed CDW deformations in NbSe\(_3\) under an applied current exceeding the threshold current \((I_T=1.3\ mA\) and \(E_T=42\ mV/cm\) at \(T=90\ K\)) as shown in figure 3-3. For fields exceeding the CDW depinning field, \(E_T\) shifts along the chain directions which corresponds to the direction of the incommensurate component of the CDW wave-vector. The shift is negligible for \(I<I_T\) and increases rapidly just above \(I_T\). For a fixed current \((I=4I_T)\) the shift increases as the temperature decreases. Near or above the threshold, a significant broadening of the CDW satellite peak perpendicular to the chain direction has also been observed in the quasi-one-dimensional material \(K_{0.3}MoO_3\) (blue bronze)\[^{[90]}\]. Such a change in the order parameter of the CDW is associated with the sliding of the CDW as observed in the transport measurements. Because the experiment was conducted at low temperature, it is expected that the amplitude excitations were frozen out and only phase excitations play the important role in changes of the order parameter \[^{[93]}\]. The plausible interpretation of the increased CDW diffraction peak width under the applied electric field exceeding the threshold field was the formation of CDW domains constructed parallel to the chain direction. A recent study by Zhang et al. \[^{[91]}\] observed a splitting of CDW satellite perpendicular to the chain direction, and the authors also ascribed this behaviour to be caused by a domain structure.

Time-resolved x-ray scattering measurements provide the evidence directly mapping the movement of the CDW satellite position when the applied electric
Figure 3.2. The threshold electric field of NbSe₃ as a function of temperature [73].
Figure 3.3. The shift in CDW peak position vs. $I/I_T$ for NbSe$_3$ [89].

field exceeds the depinning field. At a current of 29 mA and $T=70$ K, Sweetland and co-workers [90] observed the position of the CDW satellite peak to change as a function of time as shown in figure 3-4. Again this finding supports the model of a sliding charge-density wave.

Another significant finding from the investigation of x-ray scattering studies with an applied electric field is the establishment of a metastable CDW state. As mentioned above, the application of a electric field (24 V/cm in the case of ref. [92]) causes a broadening of the CDW diffraction peak. The broadening develops on a long time scale and it remains unchanged after the field is removed. The loss of order is metastable and can only be recovered by heating the sample and then cooling again in zero field.
3.3 The effects of pressure on CDWs

The study of the correlation between structural instabilities and superconductivity has been the subject of intensive research in solid state physics. A large number of materials which are semiconductors or semimetals at ambient conditions undergo a phase transition to the metallic state, or even to the superconducting state, under high pressure. The conductivity is influenced by pressure in the following four ways [94]. Firstly, the change in the interaction between the conducting electrons and the lattice as a result of the stiffening of the lattice which is in turn reflected in the electron-phonon interaction. Secondly, the change in the Fermi energy with pressure. Thirdly, due to the appearance of higher density crystallographic phases via phase transitions. Finally, the changes
in the band structure arising from the overlap between the bands or from significant changes in the electronic structure of the atoms. Because of the strong dependence of the electron-phonon interaction of the CDW distortion and the various unusual phenomena observed in low-dimensional materials, the effect of pressure has been employed to study the correlation between the CDW state and the resulting transport properties.

Measurements of the electrical resistivity under the application of pressure on the CDW material NbSe$_3$ elucidated that both CDW critical temperatures $T_1$ and $T_2$ decrease as the pressure increases, as shown in figure 3-5. This decrease was interpreted as the result of the competition between the lattice strain energy and the gain of the electronic free energy by the opening of gaps at the Fermi surface. According to the experimental findings, the temperature dependence of conductivity is more sensitive to the applied pressure below the CDW transition temperature, indicating a CDW-related unusual behaviour under applied pressure. The application of pressure results in a stiffening of the lattice and an increase of strain energy. To offset this increase in energy, the electronic energy gain must be larger for the CDW state in order to reach a stable CDW state. Consequently, the critical temperature is lowered because in the CDW state the CDW gap is enhanced as the temperature decreases [96]. It is noticeable that the second CDW transition is totally suppressed about 6 kbar (0.6 GPa). At this pressure NbSe$_3$ becomes a superconductor with a transition temperature $T_c=2.5$ K [see figure 3-6] [101][96]. Such a behaviour of the enhancement of conductivity is mainly attributed to an improved nesting of the Fermi surface under pressure, suggesting a reconstruction of the Fermi surface and therefore an increase of the density of states. The decrease of the energy gap with increased pressure for
Figure 3.5. The normalized resistivity as a function of temperature at different pressures for NbSe$_3$. a: The first CDW state ($T_1$). b: The second CDW state ($T_2$) [97].
Figure 3.6. Variation of the superconducting critical temperature of NbSe$_3$ as a function of pressure [101].
normal electron excitations is also found in other CDW materials \((\text{NbSe}_4)_{10/3}\) [98], \((\text{TMTSF})_2\text{PF}_6\) [99] and \(\text{KMo}_6\text{O}_{17}\) [100], and is responsible for the decrease of the threshold field for depinned CDWs.

It is also worth reviewing another CDW material \(2H\)-\(\text{NbSe}_2\) which has a quasi-two-dimensional character and exhibits both the highest superconducting temperature \(T_c \approx 7\) K and the lowest CDW formation temperature \(T_{CDW} = 33.5\) K under ambient conditions in the conventional CDW materials observed. By applying pressures up to 35 kbar, Berthier et al. [102] observed that \(T_c\) first increased under pressure and then nearly saturated above 30 kbar, while \(T_{CDW}\) decreased as the pressure increased as shown in figure 3-7. It is quite clear that the increase of the superconducting temperature is accompanying the decrease of the \(T_{CDW}\), but it goes to a constant (\(\sim 8\) K) when the CDW distortion is fully disrupted. From this experiment, the authors also estimated that the CDW completely disappeared for pressures higher than 36 kbar. At this pressure \(\sim 33\) kbar, a crystallographic phase change was postulated for the observed unusual transport behaviour[103].

In spite of the achievement of the enhancement of superconducting temperature by applying pressure, it is still hard to grasp the superconducting mechanism from the finite experimental data in these quasi-low-dimensional CDW materials. In summary the application of pressure suppresses the charge-density wave distortion and tends to recover the destroyed Fermi surface, but the presence of a CDW state may help to increase the superconducting transition temperature \(T_c\) under the application of pressure as observed in the case of \(2H\)-\(\text{NbSe}_2\).
Figure 3.7. The transition temperatures of $T_c$ and $T_{CDW}$ as a function of pressure for the CDW material $2H$-NbSe$_2$ [102].
3.4 Superconductivity in low-dimensional materials

There are indeed some materials exhibiting the coexistence of a CDW distortion and a superconducting state that have been observed in the $2H$ polytype layer compounds as listed in table 3-1. These layered transition metal dichalcogenides $MX_2$ ($M= V, Nb$ and $Ta; X=S$ and $Se$) are composed of close-packed sheets of metal atoms sandwiched by layers of chalcogen atoms. Each metal atom is coordinated by six chalcogens in an trigonal prismatic arrangement of covalent bonds. Measurements of resistivity show a highly anisotropic conductivity, i.e. a metallic like behaviour within the layer, indicating an anisotropic quasi-two-dimensional behaviour[106]. In these materials only a small fraction of the conduction electrons are removed by the formation of a charge-density wave, and the density of states $N(E)_F$ is still enough for the occurrence of the superconducting transition below $T_{CDW}$. Experimentally, the jump in the specific heat in $2H$-$NbSe_2$ is about 5 times larger than the predicted value by the BCS weak-coupling theory and measurements of infrared reflectivity also give a large electron-phonon coupling constant which can enhance the superconducting transition temperature, suggesting a strong-coupling in the charge-density transition[107][108].

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_{CDW}$ (K)</th>
<th>$T_C$ (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2H$-$TaSe_2$</td>
<td>122 (N-I)</td>
<td>0.14</td>
<td>[104]</td>
</tr>
<tr>
<td></td>
<td>90 (I-C)</td>
<td></td>
<td>[29]</td>
</tr>
<tr>
<td>$2H$-$TaS_2$</td>
<td>75 (N-I)</td>
<td>0.8</td>
<td>[105]</td>
</tr>
<tr>
<td>$2H$-$NbSe_2$</td>
<td>33.5 (N-I)</td>
<td>7.2</td>
<td>[102]</td>
</tr>
</tbody>
</table>

Table 3.1. $2H$ polytype layered compounds showing the coexistence of a CDW state and a superconducting state.
The coupling between charge-density waves (CDWs) and superconductivity was not only obtained from the transport measurements and the structural studies, but also evidenced by the Raman spectrum in the CDW material $2H$-NbSe$_2$ which undergoes a CDW distortion at $T_{CDW}=33.5$ K and then enters a superconducting state at $T_C=7.2$ K. Using Raman scattering Soorykumar and Klein [84] observed characteristic CDW-induced amplitude modes near 40 cm$^{-1}$ from 33 K down to 2 K, indicating the coexistence of a CDW state and a superconducting state. Neutron-scattering studies by Moncton et al. [29] also demonstrated the presence of an incommensurate CDW superlattice at $T=5$ K. The coupling was enhanced in the presence of a magnetic field. As the field strength increased, the intensity of the Raman-active modes due to the occurrence of the BCS gap decreased, while the CDW-induced modes increased in intensity. It was found that a large ratio of $\Delta(0)/k_B T_C$, where $\Delta(0)$ is the apparent energy gap at $T=0$ K in CDW’s of NbSe$_3$ and $2H$-NbSe$_2$, is dominated by the nesting condition of the Fermi surface from the high pressure transport measurements. Therefore it is possible to drive the system to a metallic, or even a superconducting state, under the circumstance of an imperfectly nested Fermi surface.

3.5 CDWs and high $T_C$ superconductors

It is still hard to construct a unique superconducting mechanism for the high-$T_C$ superconductivity to date. Considerable efforts have been devoted to aspects obtained from the copper-free superconductor bismuthates which have some remarkable similarities with the copper oxide superconductors due to the absence of the magnetic moment and the simplicity of structure; for example, a high ratio
of $T_c$ vs the density of states [109]. The bismuthate, $\text{Ba}_{1-z}\text{K}_z\text{BiO}_3$ (BKBO), has a superconducting transition temperature of $T_c \sim 32$ K which is much higher than the highest value (23 K for Nb$_3$Ge) obtained previously in conventional BCS compounds. This new system is closely related to one of the earlier superconducting oxides, $\text{BaPb}_z\text{Bi}_{1-z}\text{O}_3$, for which the maximum $T_c$ of 13 K occurs at $x \sim 0.75$. From the optical measurements a pseudo-gap induced by a charge-density wave distortion exists from the semiconducting state to the metallic state. This CDW modulation might be expected to be observed in the BKBO system. Using x-ray scattering a superstructure caused by the CDW has been observed in both semiconducting and superconducting states [see following chapters] by the author. Therefore the discovery of this new family of copper-free oxide superconductors re-establish the importance of CDWs in superconductivity. Theoretically, there have been a number of papers devoting to discussing the coexistence of a CDW state and the superconducting state based on a metallic CDW state, where the band is slightly deformed to introduce the imperfect nesting condition and a part of the Fermi surface is ungaped. Such a nested Fermi surface has indeed been observed in these high-$T_c$ cuprates [114]. This, in turn, may lead to the formation of a spin-density wave (SDW) or a charge-density wave (CDW) depending on the pairing mechanism [115], because in a CDW modulation the perturbed orbits are doubly occupied but singly occupied by up-spin or down-spin electrons for the SDW. Therefore, in the case of a CDW instability the superconducting state would be a usual $s$-wave singlet but for the SDW a $d$-wave or extended singlet would be favoured [116].

A key to understanding the mechanism of high-$T_c$ superconductivity is the symmetry of the superconducting order parameter. Up to now most of theories
Chapter 3: Charge-Density Waves and Superconductivity

developed to explain the high $T_c$ superconductivity are still based on the framework of BCS theory. One of the important results of BCS theory is the existence of a gap in the quasiparticle energy spectrum, $|\Delta(k)|$, proportional to the strength of the pairing amplitude. If this gap, $\Delta(k)$, is more or less direction independent on the Fermi surface (independent of $k$), then the system arrives at the so-called isotropic $s$-wave pairing state. In most conventional superconductors, the superconductivity arises from an electron-phonon interaction that leads to the condensation of pairs of electrons (Cooper pairs) with zero orbital angular momentum and opposite spins, and the energy gap formed in the superconducting state is very nearly isotropic in $k$ space so the gap has the same magnitude and phase in all directions, therefore they are classified to $s$-wave superconductors.

Nevertheless, some findings from the investigations of organic charge-transfer salts (Bechgaard salts) and the heavy-fermion superconductor such as UPt$_3$ suggest that a mechanism other than the electron-phonon interaction may be important in producing their superconductivity [113]. Experiments have shown that the superconducting transition temperature decreases rapidly with the addition of small amounts of nonmagnetic impurities [85]. This unusual behaviour implies that a superconductor operating via the usual $s$-wave pairing of the superconducting electrons may not be appropriate; however, it could occur with another type of pairing, such as the $d$-type pairing; where the gap $\Delta(k)$ has $d(x^2-y^2)$ symmetry in $k$-space, and it has zeros or nodes when $|k_x|=|k_y|$ (at 45° between the $k_x$ and $k_y$ axes) [110]. Thus, the energy gap (order parameter) of the $d_{x^2-y^2}$ can be formulated in $k$ space as [111]

$$\Delta(k) = \Delta_0[\cos(k_xa) - \cos(k_ya)]$$
where $\Delta_0$ is the maximum gap value and $a$ is the in-plane lattice constant. Simply speaking, the $s$-wave pairing possesses an isotropic gap and a uniform phase, but in the $d$-wave pairing has a strongly anisotropic magnitude featuring nodes along the $(110)$ directions in $k$ space and a sign change in the order parameter between the lobes in the $k_x$ and $k_y$ directions. These intrinsic differences can be used to probe the pairing of the superconductors. Using various techniques [112], such as the measurements of the magnitude of the gap by angle-resolved photoemission spectroscopy and the relative phase of the order parameter by the dc SQUID, there is growing experimental evidence for the symmetry of the pairing state of cuprates involves $d$-wave pairing.
Chapter 4

X-ray scattering with a triple-crystal diffractometer

4.1 The triple-crystal Diffractometer

In a conventional x-ray diffractometer without a crystal monochromator the finite intrinsic width of the x-ray beams prevents the detailed study of most crystallite diffraction patterns.

Consider an x-ray primary beam incident on a perfect crystal at the correct Bragg angle \( \theta \), the intensity of the diffraction peak is not only affected by the reflection of the primary beam but also by the second reflected beams being parallel to the primary within the crystal as shown in figure 4-1.

The treatment of x-ray diffraction excluding the consideration of this multiple reflection is called kinematical diffraction, which is a good approximation and has been widely applied to highly imperfect crystals consisting of very small mosaic blocks where the imperfection of the crystal smears out both effects, however,
Figure 4.1. Schematic representation of the reflection of diffracted beams

the more rigorous treatment which makes proper allowance for the reflection of these twice-reflected beams is called dynamical theory[2]. The pioneering works of the dynamical theory were developed first by C. G. Darwin, W.L. Bragg and R.W. James et al.[3] who analyzed the x-ray diffraction from a single crystal and found the integrated intensity being far from the expected value due to the extinction effect [figure 4-2] causing absorptions in the crystal, and further elucidated that this extinction effect becomes negligibly small when the mosaic blocks of crystal are very small and the disorientation of the blocks becomes sufficiently large[2][7].

Further developments of dynamical diffraction theory, as described in detail by James[3] and Zachariasen[4] et al., have explained diffraction from perfect crystals, although the treatment is necessarily complex. However, in working with crystals containing imperfections, the magnitude of the multiple reflections is
Figure 4.2. Reflection curves for a perfect crystal with absorption (top curve) and with absorption-neglected (bottom curve).
often negligible and it is difficult to distinguish the reflection from the dynamical effect unless under the condition of a highly parallel and narrow incident x-ray beam due to the intensity in the tails of the rocking curve leading to the theoretical correlation $1/\Delta q^2$[3] which arises from scattering by the surface of the monochromator or analyser, where $\Delta q$, called the momentum transfer in the reciprocal lattice space, is the vector difference between the ingoing wavevector and the outgoing wavevector. Simply speaking, the main difference on the peak profile of both theories, kinematical and dynamical scattering theory, is the former being the Gaussian shape, but the latter effect causes a non-Gaussian resolution function with large $1/\Delta q^2$ tails[11]. To some extent, the invention of the triple crystal diffractometer removes these limitations and permits a separate study of the kinematical and dynamical components of diffracted x-ray beams.

The typical arrangement of a triple-crystal diffractometer is shown in figure 4-3, in which the rotating anode x-ray source provides a high-brilliance x-ray beam, the first crystal (monochromator) collimates the incident beam, the second is the test specimen, and the third (analyser) serves to analyse the angular spectrum of the scattered radiation from the specimen. Such a setting is denoted by $(+n_m, -n_s, +n_a)$ where the "n"s indicate the order of reflection taking place in the monochromator, the sample and the analyser respectively. Experimentally, the higher-ordered diffractions from the monochromator and the analyser must be avoided so that only the first order diffraction is taken into account, and the signs of "-" and "+" indicate the directions of reflected beams from the second crystal and the third crystal as contrasted with the incident beam on the monochromator. In the case of $n_m=n_a$, the $(+1, -n_s, +1)$ setting gives a very great value for studying the widths of the reflection curves from the test crystal due to
Figure 4.3. Principal scheme of a triple-crystal diffractometer in parallel (+1,-1,+1) setting. $\Psi$ and $\Phi$ are the rotating angles of the sample and the analyser arm, respectively.

The highly parallel reflection and the absence of the dispersion effect [3].

### 4.2 The Instrumental Resolution

An important property of a triple-axis diffractometer is its resolution function, which defines the probability distribution for momentum transferring to the sample. Knowledge of the resolution function is therefore crucial for analysing and understanding the physical sense of the scattering data.

Experimentally, the resolution function is measured in the transverse ($\delta Q_\perp$) and the longitudinal ($\delta Q_\parallel$) directions by rocking the sample (only rotating the sample, and it is called a $\Psi$ scan.) or by moving the sample and the analyser arm in a ration of 1:2 ($\delta \Phi=2\delta \Psi$, namely, Theta-2theta ($\Theta-2\Theta$) scan). These measurements were performed on the vicinity of the (1 1 1) reciprocal lattice.
point for a single crystal of Si. It is clear to observe four streaks existing in the intensity distribution contour in figure 4-4, namely, the monochromator streak $M$, the main streak $Q_\parallel$, the analyser streak $A$ and the mosaic streak $S$. The existence of these effects is due to the resolution-determining elements involving the line width of the source, the reflectivities of the perfect monochromator and analyser crystals. The Darwin curve describing the reflectivity of the perfect single crystals has $\Delta q^{-2}$ tails giving rise to deviations in the incident beam. As the sample is rotated an angle of $\Phi$, these tails from the monochromator then produce a streak at an angle of $\Phi/2$ to the wavevector transfer. Since the $\Delta q^{-2}$ tails arise from the surface scattering, their effect can be reduced by using a monochromator with a rough surface, but the resolution could be reduced as well. A similar effect also happens to the analyser, but with a angle of $-\Phi/2$ to the wave-vector transfer. As it is well known that the characteristic line in the X-ray spectrum has a Lorentzian form with $\Delta \lambda^{-2}$ tails, $\Delta \lambda$ the wavelength spread of the incident beam. Furthermore it is superimposed on the continuous spectrum which has $\sim 10^{-3}$ of the intensity of the characteristic line [13]. It is important to understand the effects of the spread in incident wavelength for measurements at low levels of intensity. It has been shown that, in a triple-crystal diffractometer [12], the change in the wave-vector $\delta k$ results in a change in the wave-vector transfer

$$
\delta Q_\parallel = \delta k (2 \tan \Phi/2 - \tan \theta_M - \tan \theta_A) \cos \Phi/2
$$

$$
\delta Q_\perp = \delta k (\tan \theta_M - \tan \theta_A) \sin \Phi/2
$$

where $\theta_M$ and $\theta_A$ are the Bragg angles of the monochromator and the analyser.

In the configuration of (+, -, +) of a triple-crystal diffractometer, there is only
the spread in wavelength existing along the wave-vector transfer $Q_\parallel$ because of $\theta_M = \theta_A$. This spread effect of beams is however quite small in a highly focused x-ray source such as the synchrotron x-ray source. In figure 4-4, an intensity spread along the $S$ direction is also shown, indicating a mosaic crystal sample because, in a mosaic crystal, the reflections are from a range of orientations of the mosaic blocks, corresponding to an uncertainty in the direction of the scattering vector. In a perfect crystal this spread is small, and the peak profile is sharp.

The intensity distributions of the monochromator and analyser streaks are possible to be eliminated by the use of channel-cut crystals. By using a three reflection channel-cut crystal the $q^{-2}$ dependence of the streaks from a single reflection crystal can be reduced to $q^{-6}$ [12]. Zaumseil et al. [16] calculated the intensity distributions of a triple-crystal diffractometer with the consideration of the five reflections in monochromator and analyser, and found that the streaks coming from the monochromator and the analyser were almost suppressed and only a very sharp main streak caused by the dynamical reflection from the specimen existed in the intensity distribution contour.

The resolution function of a triple-crystal diffractometer has been widely studied in the two-dimensional reciprocal space (k-space) and can be described very successfully in terms of a Gaussian function [11]. However, the resolution function has a dependence on the degree of freedom of the diffractometer. The typical four-circle diffractometer as shown in figure 4-5 enables one to measure the reflections from the third dimension. Experimentally, the $\Omega$, $\chi$ and $\phi$ are adjusted to place the crystal in a position to diffract the incident beam with indices $(h,k,l)$ in the horizontal plane and the $2\theta$ circle places the photon counter in a position to receive the diffracted beam. If the $\chi$ circle is fixed at the position parallel
Figure 4.4. Intensity distribution in the vicinity of the (1 1 1) reciprocal-lattice point for a single crystal of Si. The inset shows the locations of the four resolution streaks due to the monochromator (M), the sample (S), the analyser (A), and the wave-vector transfer ($Q_\parallel$). The (1 1 1) reflections of perfect germanium crystals were used for both monochromator and analyser. Contour levels are shown on the right.
Figure 4.5. A four-circle diffractometer. The counter rotates about the $2\theta$ axis in one plane and the crystal may be oriented in any direction by the three axes of rotation, $\Omega$, $\chi$, and $\phi$.

to the horizontal plane, then such a configuration is equivalent to a two-circle diffractometer. The resolution of the third dimension, i.e. along the $\chi$ direction, is poorer than the other two dimensions due mainly to the divergent beam along this direction. In the two-circle mode, the divergence of the beam on the horizontal plane can be suppressed by the monochromator and the analyser.

4.2.1 High resolution scattering

In this mode, two perfect Ge(111) crystals were used to be of monochromator and analyser, and they possess a Darwin width of $\sim 0.004^\circ$. The resolution function of this configuration has been measured on a single crystal InP grown in wafer
form by Lucas et al., and gave a very high resolution of $\sim 10^{-4}\,\text{Å}^{-1}$ [12]. In spite of the highest resolution given by such an arrangement, its intensity is relatively weak, and it is not suitable for seeking the weak CDW satellites.

### 4.2.2 Intermediate resolution scattering

A perfect Ge(111) single crystal and a detector receiving slit of width $\sim 1.9\text{mm}$ were used to monochromate and collimate the CuK$_{\alpha1}$ incident and scattered beams respectively. Such an arrangement provides an instrumental resolution of $\sim 10^{-3}\,\text{Å}$ as measured on a silicon (100) wafer. This configuration was used in the experiment of chapter 5.

### 4.2.3 Low resolution scattering

A flat pyrolytic graphite crystal was used to be the monochromator, and a similar crystal was used to be the analyser. These crystals have a mosaic structure with an approximately Gaussian distribution of orientation and a mosaic spread of $0.4^\circ \pm 0.1^\circ$ (FWHM) [12]. This experimental arrangement provides a typical resolution of $\sim 0.01\,\text{Å}^{-1}$, and was widely used in the experiments described in this thesis.

### 4.3 Determination of the correlation length

In the scattering experiments, the observed reflections are a mixture of the intrinsic profile of the sample with the resolution function of the instrument. Consequently, the observed peak is related to the real-space correlation function
through a three-dimensional Fourier transform [28],

\[ I_0(\delta q) \sim \int R(r) I(\delta q - r) dr \]

\[ I_0(\delta q) \sim \int R(r) dr \int e^{i(\delta q - r)z} (e^{i[\phi(z) - \phi(0)]}) dz \]

where \( I_0 \) is the measured intensity at momentum transfer \( \delta q \), and \( R(r) \) is the measured resolution function having a three-dimensional character. Experimentally, the resolution function can be measured from a perfect Si crystal or a perfectly grown film sample, and it can be fitted with a Gaussian form, depending on the scattering geometry and the quality of crystals [11][5]. In some circumstances, for instance the presence of the poor resolution along the longitudinal and the \( \chi \) direction shown in figure 4-5, the dimensionality of 3 can be effectively reduced to 1 [28]. The measured line shape is then given by the one-dimensional convolution of the intrinsic scattering with the scattering direction resolution function,

\[ I_0(\delta q_t) \sim \int R(r_t) dr_t \int e^{i(\delta q_t - r_t)z} (e^{i[\phi(z) - \phi(0)]}) dz \]

where subscript \( t \) indicates the scattering direction. In this one-dimensional case, the Fourier transform of a pure Lorentzian function in reciprocal space is an exponential correlation function in real space, \( \langle e^{i[\phi(z) - \phi(0)]} \rangle \sim e^{-z/l} \). Thus the correlation length \( l \) can be obtained through the fitting formula,

\[ I_0(\delta q_t) \sim \int R(r_t) dr_t \int e^{i(\delta q_t - r_t)z} e^{-z/l} dz, \]
and it is the inverse of the Lorentzian width. In practical, if the width of the reflections of the sample is far larger than that of the resolution function, a simple Lorentzian function

\[ I(\tau) \sim \Gamma / [(r - \Delta r)^2 + \Gamma^2], \]

can be directly fitted to the data, where \( \Gamma \) is the Lorentzian width, because the resolution function has only a little effect in the peak width measured.

4.4 X-ray reflectivity

At sufficiently small incident angle, x-rays undergo total external reflection from a even surface and their penetration depth is greatly reduced. Therefore this technique can be used to study the thickness and the interface roughness of the crystalline or the amorphous films.

Consider x-ray travelling in a glancing angle to a \( N \) stratified homogeneous media having smooth boundary interfaces, Parratt [10] deduced a recursion formula for the reflectivity by solving Maxwell's equations,

\[ R_{n-1,n} = a_{n-1}^4 \left[ \frac{R_{n,n+1} + F_{n-1,n}}{R_{n,n+1} F_{n-1,n} + 1} \right] \]

\[ R_{n,n+1} = a_n^2 \left[ \frac{E_R^N}{E_n^N} \right] \]

\[ F_{n-1,n} = \frac{f_{n-1} - f_n}{f_{n-1} + f_n} \]

where \( a_n \) is the amplitude factor for half the perpendicular depth \( d_n \), and

\[ f_n = [\Psi^2 - \Psi_c^2(n)]^{1/2} \]
where $\Psi_c(n)$ is the critical angle of the $n$th layer and it can be converted to mass density. The ratio of reflected to incident intensity, $I_R/I_0$, is $I_R/I_0 = \left|E^{R_1}/E_1\right|^2$, experimentally, therefore information of the layers can be obtained by studying the reflected intensity changed in the function of the incident angles $\Psi$.

### 4.4.1 A study case in the use of x-ray scattering: a strained layer semiconductor

The growth of an hetero-epitaxial layer on a substrate will in general produce a strained structure due to the mismatch of the lattice parameters or differential thermal conductivity between the two layers. Such effects are explored in the design of semiconductor devices due to their influence on the electronic and the structural properties, and the internal strain also within a thin buried layer quantum well which confines the mobility of electrons [8].

The strained structure has a strong correlation with the layer thickness. The strain increases as the layer thickness does, but when the thickness exceeds a critical value, it often produces misfit dislocations which relax the strain and hence effect the optoelectronic properties of the materials. It is therefore extremely valuable to have techniques capable of observing the structural perfection of interfaces so that the growth conditions can be optimised to produce heteroepitaxial thin films with the highest quality.

In this study case, two perfect germanium (111) single crystals were used for both monochromator and analyser, respectively. Such a configuration provides a Darwin width of $\sim 5 \times 10^{-4} \text{Å}^{-1}$. The strained layer film was grown by Dr. E. Macdonald, University of Wales, and was composed of both of GaSb and InAs.
layers, i.e. a buffer layer GaSb \(\sim7000\text{Å}\) was grown on a GaSb (100) substrate and then capped with a thick layer of InAs (\(\sim5000\text{Å}\)) and finally covered with a thin GaSb layer [figure 4-6].

In order to examine the interface between the layers and the surface, both methods of x-ray reflectivity and glancing-incidence x-ray scattering were used. The reflection of x-ray from surfaces and layered structure was first studied by Kiessig [9] and later by Parratt [10] and many others [11]. In this study case the data analysis of the reflectivity were based on the ideas proposed by Cowley et al.[11] who followed the simpler treatment of Parratt [10] and demonstrated that the specular reflectivity, \(T\), of a layered system is in the form of \(T=R\Psi^4\), where \(R\) is the reflected intensity of x-ray beams from a mirror surface containing information about the charge density variation as a function of depth, roughness and layer thickness. In this model, the period of the oscillation gives an accurate measure of the layer thickness and the amplitude of the oscillation is a measure of the difference in the electron density between the layers. The information of the roughness comes from the relative amplitude of the oscillations. By using the triple-crystal diffractometer, the improved wave vector resolution permits the observation of weak scattering from the layered structure, away from Bragg reflections, which contains detailed structure information [14] but it is only sensitive to the crystalline structure. However, by combining both methods of x-ray reflectivity and glancing-incidence x-ray scattering, the layered structure can be studied in detail.

The sample was mounted on a triple-crystal diffractometer with the normal direction \(<1 0 0>\) of the GaSb substrate. In making the reflectivity measurements the adoption of an analyser crystal defines the scattering angle, \(\Phi\), with
Figure 4.6. A schematic view of strained layers
an accuracy of better than 0.005°. By rocking the sample at positions of $\Phi=2\Psi$, where $\Phi$ the scattering angle and $\Psi$ the sample orientation, the integrated intensity of the reflected beam from all parts of the sample was obtained [14]. On the diffraction measurements the $(\bar{2} 2 4)$ reflection, where the Bragg angle is $76.5^\circ$ and the incidence angle is approximately $4.21^\circ$, is particularly suitable for glancing-incidence x-ray diffraction studies because of its sensitivity to the surface of the sample.

As displayed in figure 4-7 the reflectivity data were fitted with three layers and are plotted on a logarithmic scale over four decades of intensity. It shows a steadily decreasing intensity as $\Psi$ increases, which is caused by the surface roughness. The oscillations in $T$ arise from the interference between waves reflected from interfaces, and the period of the oscillation gives an accurate measurement of the layer thickness. The amplitude of the oscillations is a measure of the difference in the electron density between layers. For a chosen model, the variable parameters of the theory were fitted to the data using least-squares refinement of a recursion formula of the reflectivity, the experimental deviations were dealt with in terms of the statistical errors, and are listed in table 4-1, where the thickness of the InAs layer was treated as infinite with respect to the penetration depth of x-rays (x-rays penetrate only tens of micrometres through most materials), and the layer 1 was caused by oxidation. The high resolution triple-crystals diffractometer provides the two-dimensional intensity distribution of scattered x-rays in an area of reciprocal lattice space. Figure 4-8 shows such a contour pattern around the $(\bar{2} 2 4)$, in which two stronger reflections, $(\bar{2} 2 4.045)$ and $(\bar{2} 2 4)$, are the Bragg reflections coming from the InAs and the GaSb. The difference of 0.045 also indicates a distortion in the lattice parameter of InAs,
Figure 4.7. The reflectivity intensity multiplied by $\Psi^4$ plotted on a logarithmic scale against Psi ($\Psi$).
Figure 4.8. The two-dimensional intensity map around the (2 2 4) Bragg peak.
Table 4.1. These parameters were obtained from fits to the reflectivity curve shown in figure 4-7.

4.5 Conclusions

The x-ray reflectivity technique has been used to non-destructively characterise heterostructures. In the present study, the oscillations curve in the x-ray reflectivity as a function of grazing incidence angle contains information about conditions at the top surface and buried interface. By combining data obtained from x-ray
Figure 4.9. The linear scan through the \((\bar{2} \bar{2} 4)\) direction. Fringes can be observed on both sides of the main peak.
reflectivity and grazing-incidence diffraction, a non-crystalline layer of 33 Å was observed between layer 2 (GaSb) and layer 3 (InAs).

Neutron, x-ray and electron beams can be used to study the structural characterization of materials, and they have quite different properties. In fact, each has unique advantages and they supplement one another to a remarkable degree. A neutron is electrically neutral, and causes no polarization of the electron clouds which enables neutron beams to penetrate several centimetres through most materials. Experimentally, because neutrons are scattered mainly by the atomic nucleus and the scattering amplitude does not show a smooth dependence on the atomic number of the atoms, neutron scattering is particularly useful in locating light atoms in crystals and studying the magnetic ordered structure of materials. On the other hand, neutron beams are much weaker in intensity than x-ray beams, so a larger single crystal is required in neutron diffraction. For electron diffraction, electron beams interact strongly with the electrons in materials and also ionize atoms. These effects cause a short penetration depth. Electron diffraction is therefore well suited to the study of thin surface layers because of the occurrence of diffraction only over a depth of a few hundred Å or less, but the result are heavily influenced by the multiple scattering of the electrons. In contrast, x-ray scattering has advantages over both neutron and electron beams in many ways; a weaker interaction with the surface, higher resolution with a comparable intensity and easy access to the source. Such merits make x-ray scattering of wide utility in the study of the structure of materials.
Chapter 5

Modulated structures induced by the CDW in the Ba$_{1-x}$K$_x$BiO$_3$ series

5.1 Introduction

The discovery of the high-$T_c$ superconductor, Ba$_{1-x}$K$_x$BiO$_3$, has introduced new aspects into the mechanism of high-$T_c$ superconductivity as compared to most of the superconductors containing copper-oxide layers. With a low density of states and a transition temperature of $\sim$34 K which is considerably higher than that of conventional superconductors, the BKBO superconductor has been regarded as a high-$T_c$ superconductor. The properties of copper-oxide layers and magnetic moments have been proposed as playing the crucial roles in these perovskite-derived cuprates. However, it has been shown that the high-$T_c$ mechanism is not related to the two-dimensionality of Cu-O planes or magnetism, since the bismuthate superconductors were discovered. Instead, the modulation caused by the formation of the charge-density wave, whose origin is the charge redistribution
due to the distortions, has been taken into account for the superconducting and the semiconducting properties in the bismuth-oxide superconductors.

The modulated structure in the single crystal $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ has been investigated by single-crystal x-ray scattering on a variety of compositions. Attention has been focused on the modulated structure observed by electron diffraction in the [110] direction. The modulation is commensurate with the host lattice producing a $\sqrt{2}a_p\times\sqrt{2}a_p\times2a_p$ supercell, which is widely believed to be due to the ordered disproportionation between non-equivalent $\text{Bi}^{3+}$ and $\text{Bi}^{5+}$ valence ions. In this study, the modulated structure which is caused by the formation of a charge density wave has been confirmed to extend from the semiconducting composition, $x\sim0.15$, to the superconducting composition, $x\sim0.4$.

5.2 Crystal structures of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$

The crystal structure of the parent compound of BKBO, $\text{BaBiO}_3$, is a member of the perovskite family. It is a member of the family of the generalized formula $\text{ABX}_3$ and structurally consists of cubes in which the A-cations occupy all eight corners, and the B-cations lie at the centre of each cube and the X-anions are at the midpoints of the cube's 6 faces [figure 5-1]. As a consequence of substitutions with different cations or anions, the adaptable perovskite structures give rise to materials that have a wide range of physical properties. It has been shown, that all the high $T_C$ superconductors, cuprates and bismuthates possess a perovskite or modified perovskite as the structural base.[see figure 5-2]

Without considering distortions, the crystal structure of $\text{BaBiO}_3$ is primitive cubic with the space group $\text{Pm}\overline{3}\text{m}$ [117]. In this situation there is only one $\text{Bi}^{4+}$
Figure 5.1. The typical perovskite crystal structure.
Figure 5.2. The crystal structures of high $T_c$ superconductors, a: cuprate (La$_{1.85}$Sr$_{0.15}$CuO$_4$), the room temperature tetragonal phase. b: Bismuthate (Ba$_{0.6}$K$_{0.4}$BiO$_3$), the undistorted structure.
in the unit cell. A metallic state would be expected because of the properties of a half-filled band. Experimentally, BaBiO$_3$ is a semiconductor. Using neutron powder diffraction and x-ray crystal diffraction, Cox [117], Pei [118] and Schneemeyer [119] et al. have found that there are two different Bi sites existing per unit cell, namely BaBi$_{1/2}$$^{+3}$Bi$_{1/2}$$^{+5}$O$_3$. The octahedra about the B ions are still regular but no longer equivalent, reflecting the different sizes of the two cations at B sites, Bi$^{3+}$ and Bi$^{5+}$. This disproportionational distortion creates a commensurate CDW which opens a gap at the Fermi surface and accounts for the semiconductivity. The distorted structure in the BaBiO$_3$ is formed not only from the breathing-mode distortion in which oxygen atoms go toward or away from the centre of the each octahedra [figure 5-3] but also involves a tilting distortion of the rigid octahedra along the [110] axis with an average tilt angle of 10.3° at T=295K [118]. This tilting increases as the temperature decreases [figure 5-4]. Such a combination of both distortions gives a body-centered monoclinic phase of space group $I2/m$. Upon doping, as shown in table 5-1 various structures have been found using different techniques. The differences between the various structures depend on the presence of the tilting distortion or the breathing-mode distortion. The structure having only the octahedral tilting distortion is the $I2/m$ phase, gives rise to the orthorhombic $Ibmm$ phase and was identified in the composition range from 0<x<0.3 at T=295K. However, Schneemeyer et al. also reported an orthorhombic $Immm$ structure for a single crystal of composition Ba$_{0.96}$K$_{0.04}$BiO$_3$. This structure contains an asymmetric breathing-mode distortion without the octahedral tilt. As described in Pei’s studies the $Ibmm$ structure contains superlattice reflections that can be indexed on a body-centered $\sqrt{2}a\times\sqrt{2}a\times\sqrt{2}a$ supercell.
Figure 5.3. A schematic representation of the breathing-mode distortion in BaBiO$_3$. Arrows show that oxygen atoms go toward or away from the Bi$^{3+}$ and Bi$^{5+}$ sites.
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Table 5.1. Lattice parameters in the $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ system [118].
Superconductivity in the BKBO series is observed in an undistorted cubic $Pm\bar{3}m$ structure with the maximum $T_c$ of 30K being achieved at $x\sim0.37$ close to the phase transition boundary. This disappears dramatically upon crossing the first order phase transition into the semiconducting orthorhombic phase ($Ibmm$) when the potassium concentration is decreased [figure 5-5]. As indicated in the literature the superconducting compound maintains this undistorted cubic structure down to the superconducting transition temperature [124] [118] [119].

There was not any direct evidence from x-ray or neutron diffraction patterns to support the existence of a CDW modulated structure in the BKBO series, (even in the BPBO series), but a cubic $Fm\bar{3}m$ structure resulting from the elimination of the tilting distortion while maintaining the breathing-mode distortion is suggested in the band structure calculation as proposed by Mattheiss [120]. This
Figure 5.5. The phase diagram of Ba$_{1-x}$K$_x$BiO$_3$ as a function of both potassium content and temperature [127].

pure breathing-mode distortion leaves the non-equivalent Bi$^{3+}$ and Bi$^{5+}$ ions and leads to the presence of a 2a×2a×2a superstructure.

5.3 Modulated structures in the BKBO

Superconductivity in the BKBO compound is observed in the cubic (Pm$\bar{3}$m) phase, and the maximum T$_c$ of 30K is achieved at x≈0.37 [figure 5-6] close to the phase transition boundary and disappears dramatically upon crossing the phase transition into the semiconducting orthorhombic (Ibmm) phase when the potassium concentration is decreased. Owing to the simple structure and the high transition temperature, the BKBO compound provides a model system for investigating superconductivity in metal-oxides. The crystal structure
of the parent compound BaBiO₃ is distorted by the BiO₆ octahedral tilts, and the breathing-mode distortions which cause a commensurate charge-density-wave (CDW) opening up a gap at the Fermi surface and also explaining the semiconducting property in this compound. Such a CDW energy gap has been observed in the spectrum of optical conductivity from the semiconducting state extending to the superconducting state. Recent research has focussed on the interaction between CDW's and superconductivity in the substituted series BaPb₁₋ₓBiₓO₃ (BPBO) and Ba₁₋ₓKₓBiO₃ (BKBO). The BPBO system exhibits superconductivity with \( T_c \) varying from 0.45 K for \( x=0 \) to 13 K for \( x=0.25 \). Above \( x=0.3 \) the system is semiconducting due to the commensurate CDW as in the parent material BaBiO₃. The link between the CDW and superconductivity is demonstrated by the highest \( T_c \) occurring with a composition adjacent to an instability.
caused by the CDW opening a gap in the Fermi surface. The relationship has been further observed by optical reflectivity measurements by Tajima et al. [122] who showed that the CDW energy gap exists as what they called a "pseudogap" in the metallic state and develops smoothly with concentrations of Pb into a "true" gap for x > 0.3. In a subsequent theory proposed by Machida et al. [123], the enhancement of Tc results from a gap-edge singularity associated with the charge-density state which increases the density of states at the Fermi surface.

The evidence for a CDW relies entirely on electron diffraction studies. The initial study of Pei et al. [125] found incommensurate satellites along the <110> directions in the semiconducting phase about the pseudocubic Bragg reflection positions. The positions of the satellite reflections varied with the potassium concentration prompting the speculation that there existed an incommensurate Fermi surface-induced CDW. Hewat et al. [126] also observed this incommensurate modulation and a similar potassium dependence but found that the satellites appeared only after irradiation by the high energy electron beam and hence concluded that such features were not an intrinsic feature of the semiconducting phase. Additional electron diffraction studies by Pei confirmed the linear dependence of the incommensurate wavevector with the potassium content but such satellites could not be observed by neutron diffraction [118] [124]. The most detailed electron diffraction study by Verwerft et al. [127] confirmed the presence of incommensurate satellites in both the semiconducting and superconducting phases.

Although electron diffraction is sensitive in detecting superstructures, it also has the unfortunate possibility of inducing structural changes due to the high energy irradiated electron beam impinging on the sample. This is a particular
problem in many metal-oxides with high oxygen mobility and particularly in studies of high Tc superconductors where the properties are highly dependent on oxygen vacancies. X-ray diffraction is less surface sensitive and cannot cause such damage. It is therefore a preferred technique. In this chapter, I describe the first observations of a modulated structure caused by the formation of CDWs using x-ray scattering techniques.

5.4 Experiment

The single crystals with the superconducting compositions were grown by Dr. H. Y. Tang et al. using low-temperature, isothermal, and isopotential electrochemical deposition. This technique produces high quality large crystals from which single crystals were collected\[128\]. The samples were characterised by magnetic measurements. The superconducting composition (sample A with a size of $\sim2\times2$ mm$^2$, $x\sim0.4$) displays a on-set temperature of 30 K but with a broad transition width of $\sim8$ K. A second crystal grown by a similar technique by Prof. Barilo [129] with a lower potassium content (sample B with a size of $\sim1\times2$ mm$^2$, $x\sim0.15$) was semiconducting and did not show a superconducting transition down to 5 K. I also checked a lot of samples, more than a hundred, obtained from other growth groups, using back-reflection Laue method, but most of them showed a mess of spots in their Laue patterns. Only the few small samples used in this experiment showed a clear Laue pattern indicating a better quality. Experiments were carried out by using a two-circle triple-crystal diffractometer. The x-ray beam was produced from a rotating-anode generator operating at 2.7 kW with a Cu target. A flat pyrolytic graphite monochromator was used to provide a monochromatic
incident beam, and a similar analyzer was used to define the scattered beam. The crystals were examined and aligned using Laue diffraction before being mounted on the diffractometer and were chosen with the surface normal to [0 0 1] direction and the [1 1 0] in the scattering plane. Such an arrangement gives a relatively poor resolution of ~0.6° full width at half maximum of the Bragg peak (3 0 0) for sample A but very high intensities. The beam size was reduced by primary slits down to ~1×2mm² and the crystal was translated until a relatively clean profile of the Bragg peaks was obtained. Such a procedure ensures scattering is observed only from one large crystal within the sample. Low temperature measurements were performed by mounting the sample in a helium closed cycle cryostat with a temperature stability of ±0.01 K.

5.5 Results and Discussion

One dimensional scans through the principal Bragg peaks of the superconducting composition (sample A) are shown in figure 5-7. The lattice parameter was refined from these to a value of 4.28±0.005Å. This value has a relatively large uncertainty due to the low number of Bragg reflections accessible with CuKα radiation in reflection geometry. Nevertheless the lattice parameter confirms that the concentration of potassium is approximately ~0.4 and the results confirm the lattice to be cubic. A two dimensional contour plot of the x-ray scattering centered on the (300) Bragg peak revealed weak superstructural satellites at (2.5 0.5 0), (2.5 0 0), (2.5 0.5 0), (3 0.5 0), (3 0.5 0), (3.5 0.5 0), (3.5 0 0) and (3.5 0.5 0), (see figure 5-8). These peaks have an intensity of typically $10^{-4}$ times that of the Bragg peaks. Other weak peaks (such as that at (3.31
Figure 5.7. Theta-2theta scans through the principal Bragg reflections (200), (300), (410) and (310) using a high resolution germanium (111) monochromator and a detector slit of ~0.3mm.
Figure 5.8. An isointensity contour plot of the x-ray scattering intensity around the (300) Bragg peak from a superconducting composition (sample A, x=0.4) at room temperature using pyrolytic graphite monochromator and analyser crystals. The contour levels displayed to the right were chosen to accentuate the weaker features.
Figure 5.9. One dimensional scans along the [1 0 0] direction through the (300) Bragg peak and the superstructure satellites (3.5 0 0), (3 0.5 0) and (2.5 0.5 0) at T=295 K. The solid lines are guides to the eyes.
0.4 0)) were occasionally observed but these were always irreproducible, being absent after further polishing using diamond paste or in other crystals with the same composition. This leads us to believe that these spurious peaks are due to small misorientated crystallites within the sample. Scans through some of the superstructure satellites are shown in figure 5-9 which confirm their existence. The width of the superstructure peaks is comparable to the main Bragg peaks and they are resolution limited.

The superstructure satellites observed as shown in figure 5-8 were always found close to half integer positions. Comparison of the superstructure satellites with the position of nearby integer Bragg peaks might suggest that the superstructure satellites are slightly off the half integer positions. The deviations, however, are small compared to the instrumental resolution (e.g. peaks were found at (3.485 0.01 0) and (2.505 0.5 0)). In order to ensure whether such small deviations are true or merely caused by crystal centring errors further studies are needed using higher resolution and will be reported in the next chapter.

Low temperature studies were also completed and gave very similar results to those obtained at room temperature. Figure 4-10 displays the x-ray scattering around the satellites (3.5 0 0), (3 0.5 0), and (2.5 0.5 0) at 15K. These data were obtained at T=15K without realignment before measurement. Superstructure satellites can be observed nearby half integer positions indicating that the charge density wave still exists even in the superconducting state.

In order to make sure that the superstructure observed is not sample dependent, measurements on other samples grown by the same group and crystals obtained from different groups were also taken. Figure 4-11 shows the same results from a crystal obtained from Russia, in which superstructure satellites
Figure 5.10. Isointensity contour plot of the x-ray scattering intensity around the (3.5 0 0), (2.5 0.5 0) and (3 0.5 0) superstructure satellites at $T=15$ K. Such results confirm the existence of the CDW in the superconducting phase.
Figure 5.11. An isointensity contour plot of the x-ray scattering intensity around the (300) Bragg peak from a similar composition (x=0.4) crystal from Russia. Superstructure satellites at half integer positions are observed (arrowed) at (3.5 0 0), (3.5 0.5 0) and (3 0.5 0) at T=295 K. Additional scattering in the <010> direction around the (300) Bragg peak is due to the larger mosaic width.
around half integer positions still can be seen. These results provide evidence that the observations are a natural feature of $\text{Ba}_{1-\varepsilon}\text{K}_\varepsilon\text{BiO}_3$ crystals and not a peculiar effect of some particular microstructure found in one crystal.

Attention was also paid to search for incommensurate satellites reported at $q=(6-\epsilon)\langle 110 \rangle$, where $\epsilon$ is the incommensurability which changes with the concentration of potassium, by electron diffraction [125]. Scans taken through the $\langle 110 \rangle$ direction failed to find any evidence of enhanced x-ray scattering. Any such satellites would thus be at least an order of magnitude weaker than the commensurate superstructure reflections mentioned above. In this respect, such scans are in agreement with the synchrotron study by Wochner et al [130] that such incommensurate satellites do not exit in unirradiated samples. However, we therefore believe that the additional scattering observed in the electron diffraction studies (which increases in intensity under irradiation) was caused by electron beam damage to the samples. In the electron-diffraction patterns of Verwerft et al [127] and of Zhou et al [131] it can be seen that in addition to the satellites there are also satellites at $(0.5\ 0.5\ 0)$, $(1.5\ 0.5\ 0)$ and $(0.5\ 1.5\ 0)$ etc.. No satellites can be seen on their published diffraction patterns at $(1.5\ 0\ 0)$, $(2.5\ 0\ 0)$ etc. and the authors fail to discuss the origin (or even the existence) of such commensurate satellites.

The results above indicate that the charge density wave can coexist with the superconductivity in BKBO. In general, superconductivity and CDW's suppressing superconductivity and vice versa [135]. Such is the case in the chevrel phases $\text{BaM}_6\text{S}_8$ and $\text{EuM}_6\text{S}_8$ which are not superconductors due to the presence of the CDW which opens a gap over the entire Fermi surface [133]. However there are a small number of systems where imperfect nesting of the CDW can allow the
coexistence of superconductivity in a CDW distorted structure. The quasi-one-dimensional compound NbSe$_3$ undergoes two CDW transitions at $T_1=145$ K and $T_2=59$ K [97][87][134][96] The latter transition is responsible for the presence of a superconducting state at low temperature ($T_c=2.8$ K) and high pressure ($P=5.5$ kbar). This phase has a partially deformed Fermi surface caused by imperfect nesting of the CDW which leaves remaining pockets of electrons and holes at the Fermi surface. Similar effects have been inferred in the layered compounds 2H-NbSe$_2$ from Raman scattering measurements [135][136] and in 1T-TaS$_2$ [137]. Theoretical studies have shown that metallic CDW states can be formed by a Peierls distortion within the framework of the BCS model [138] when the CDW is imperfectly nested.

A structural transition from the cubic ($Pm\bar{3}m$) to the orthorhombic ($Ibmm$) phase occurs at low temperature for $x\sim0.37$, corresponding to the onset of bulk superconductivity [118]. It is still not clear whether such a structural transition is accompanied with a change in the superstructure. In order to compare the differences between the modulated semiconducting state and the modulated superconducting state, measurements on a semiconducting crystal with $x=0.15$ were performed. As shown in figure 5-12, overall there is considerable similarity to the results obtained from the metallic or superconducting compositions (Figure 5-8 and 5-11). The crystal quality is good as evidenced by the reduced mosaic width, in spite of the presence of other peaks (e.g. (2.825 0.355 0)) which are believed to be due to misorientated crystallites in the sample. Again, superlattice reflections can be seen to surround the (300) Bragg peak at half integer positions along the $<100>$, $<010>$ and $<110>$ directions. Figure 5-13 shows scans through the (3.5 0 0), (2.5 0.5 0) and (3.0.5 0) peaks confirming their existence, including the
Figure 5.12. A contour map of the x-ray scattering intensity around the (300) Bragg peak from a semiconducting composition (sample B, x=0.15) at T=295 K.
Figure 5.13. One dimensional profiles along the <100> direction of the (300) Bragg peak and the (3.5 0 0), (3 0.5 0) and (2.5 0.5 0) superstructure satellites from the semiconducting composition at T=295 K. The solid lines are given as a guide.
Figure 5.14. A one dimensional scan along the $<100>$ direction from (100) to (400) displaying the Bragg peaks, superstructure satellites, (1.5 0 0), (2.5 0 0) and (3.5 0 0), and additional weak features at (1.67 0 0), (2.67 0 0) and (3.67 0 0).
latter peak, (3 0.5 0), which can not be seen in figure 5-12 because of its lower intensity. However the positions of the superlattice reflections are either on, or very close to the half integer positions; such a deviation still cannot be detected by present resolution standards. The major difference between the two compositions was found by a scan in the <100> direction as shown in figure 5-14 which was obtained with a longer counting time than the grid scan scan of figure 5-12 and displays additional peaks at (1.67 0 0), (2.67 0 0) and (3.67 0 0) which are not present in the metallic or superconducting state. Such peaks are evidence of a larger supercell or incommensurate structure.

Chaillout et al.[139] studied oxygen deficiency in BaBiO$_3$-$\delta$ using x-ray and electron diffraction and observed incommensurate satellites with wavevectors $\vec{G}_1=0.34<100>$ and $\vec{G}_2=0.34<010>$ in the (hk0) reciprocal plane around the Bragg spots. Superlattice reflections in positions, (1.67 0 0), (2.67 0 0) and (3.67 0 0), are thus in close accord with these incommensurate satellites with the wavevector $\vec{G}_1$, but the search for other satellites such as (1.33 0 0) or (2.33 0 0) was unsuccessful, but this may be simply due to their lower intensity. Other satellites such as (3 0.33 0) could not be reliably found because of the large mosaic streak from the neighbouring Bragg reflection. An estimate of the correlation length along the transverse and longitudinal directions of the (3.67 0 0) was also undertaken as displayed in Figure 5-15. The FWHM of the (3.67 0 0) seemed to be greater than that of the CDW superlattice peak (3.5 0 0), which also indicates both superstructure arising from different origins. Scans along both directions gave a estimated ratio of correlation length, $\varepsilon_\parallel/\varepsilon_\perp$~2.2, which is subject to large error due to the low intensity of the incommensurate peak. Such a value might
Figure 5.15. One dimensional scans along a.) the longitudinal direction <100> and b.) the transverse direction <010> through the (3.67 0 0) peak.

indicate a short range order with an anisotropic correlation length due to quasi-one-dimensional fluctuations in the a*b* plane. The parent compound BaBiO$_3$ is monoclincally distorted due to octahedral tilting and breathing mode distortion. Schneemeyer et al.[119] have pointed out that substitution of potassium on the barium sites gradually suppresses the tilting distortion, thus implying that the incommensurate superstructure is probably induced by such a tilting distortion. The effect of this additional modulation on the transport properties is still unclear. However, it is known that in the single-particle energy spectrum the incommensurability creates a set of discrete levels which may enhance the band gap at the Fermi surface so that the conductivity is decreased[140].
Chapter 6

An incommensurate CDW in the superconductor Ba$_{0.6}$K$_{0.4}$BiO$_3$

6.1 Introduction

In the previous chapter a superlattice resulting from the formation of a charge-density wave was invoked to explain the presence of x-ray scattering at half integer positions in both metallic and semiconducting compositions of BKBO. The measurements were obtained using a graphite monochromator and analyser and revealed that the charge-density wave state can exist even within the superconducting state at low temperatures. Such an behaviour is quite unusual as compared with most quasi-low-dimensional materials, e.g. the niobium triselenide NbSe$_3$ in which both superconductivity and the presence of a CDW are incompatible [96]. Studies of superconductivity in charge-density wave materials have suggested the presence of a CDW state which results from an imperfectly
nesting Fermi surface where the incompletely destroyed electron and hole pockets still provide conduction electrons. In the cuprate, (La\(_{1-x}\)A\(_x\))\(_2\)CuO\(_4\) (A=Sr, Ba, Ca) and YBa\(_2\)Cu\(_3\)O\(_{6+x}\) and bismuthate superconductors, BaPb\(_{1-x}\)Bi\(_x\)O\(_3\) and Ba\(_{1-x}\)K\(_x\)BiO\(_3\), the nesting effect of the Fermi surface has been proposed to play a crucial role in the transport behaviour [154][155][156]. A nested Fermi surface can be responsible for the formation of a charge-density wave modulation. Recent theoretical and experimental studies have investigated the occurrence of a charge-density wave instability and its relationship to superconductivity. In the investigation of such a relationship it is important to determine the CDW wave vector and its correlation length. In the model proposed by Fröhlich built on the framework of the Peierls transition, the incommensurate CDW was described as being able to travel unattenuated and therefore implying an infinite conductor [83]. T. M. Rice and L. Sneddon, and E. Jurczek and T. M. Rice also demonstrated how the conductivity changes with substitutions of lead on the bismuth sites in BPBO oxides, which was based on the consideration of a localized CDW modulation [145][146]. Given the uncertainty in the identification of the CDW wave-vector in previous low resolution measurements, an attempt at determining the wavelength and the peak width of the CDW modulation was attempted using higher resolution x-ray scattering.

### 6.2 Experiment

Basically, this experimental configuration was the same as the previous experiment, except that a perfect Ge(111) single crystal and a detector receiving slit of width ~1.9mm were used to monochromate and collimate the CuK\(_{\alpha1}\) incident
Figure 6.1. A Q-scan along the Bragg peak (0 0 4) of a silicon (1 0 0) wafer provides an instrumental resolution of $\sim 10^{-3}$ Å.

and scattered beams respectively. Such an arrangement provides an instrumental resolution of $\sim 10^{-3}$ Å as measured on a silicon (100) wafer [figure 6-1]. The sample was mounted in a helium closed cycle cryostat with a temperature stability of $\pm 0.01$ K. The crystal was mounted in such a way that the scattering plane was $a^* \times b^*$.

6.3 Results and Discussion

In the previous study CDW satellites were observed at half-integer positions in the hk0 plane. Using the higher resolution such satellites were found to be composed of two peaks symmetrically displaced from the [1 0 0] axis. Figure 6-2 shows a contour map of the scattered intensity around (1.5 0 0). The two peaks are observed at (1.494 -0.012 0) and (1.489 0.011 0). Similar results were obtained
Figure 6.2. An isointensity contour plot of the x-ray scattering intensity of the CDW satellite around (1.5 0 0) from Ba_{0.6}K_{0.4}BiO_3 at T=295 K. The contour intensities (counts per 50 seconds) are shown on the right.
around (2.5 0 0) and (3.5 0 0) [6-3]. Off-axis reflections were observed using lower resolution but have insufficient intensity for observing them with this improved resolution. Combining the results, the positions of the CDW satellites seem to be displaced from integer Bragg peaks by 0.494(2)a* and ±0.011(3)b*. Somewhat surprisingly no satellites could be located around 1.506a*±0.011b* which would be expected to be observed. In a modulated structure, the modulated wave vectors can be expressed as

\[ \vec{Q}_t = h \vec{a}^* + k \vec{b}^* + l \vec{c}^* \pm \vec{q}_0 \]

where \( q_0 \) is the located position of the superstructure in reciprocal space. In this study \( q_0 \) was located at 0.494a* and 0.011b*, therefore both values indicate the presence of relative wave vectors at positions (0.494 0.011 0), (0.494 -0.011 0), (1.506 0.011 0) and (1.506 -0.011 0).

Such findings lead to the suggestion of a CDW domain structure which is an intensely interesting topic in the investigation of the CDW modulated structure[35]. Provided that the origin of this splitting is due to the domain distribution coming from the host structure, one should also see the same phenomena in the Bragg peaks [157]. After many detailed searches, no splitting of the Bragg peaks could be observed. The symmetry of the two satellites around the \((h 0 0)\) direction is very similar to the observation of a split superlattice peaks in the CDW material \(K_{0.3}MoO_3\) under an applied electric field and suggests they originate from CDW domain splitting [91]. In this experiment it could occur because the CDW is incommensurate and not aligned along the cubic directions. Scans through the CDW satellites demonstrate that they are broadened relative to nearby Bragg
Figure 6.3. An isointensity contour plot of the x-ray scattering intensity of the CDW satellite around (3.5 0 0) from Ba_{0.5}K_{0.4}BiO$_3$ at $T=295$ K. The contour intensities (counts per 50 secs) are shown on the right.
peaks indicating a small domain size limiting the correlation length. The attribution of the weak supercell scattering to a CDW is supported by further measurements under a magnetic field. The application of the magnetic field causes a dramatic increase of the splitting. Identical results were also obtained from observations of other superlattice reflections such as (3.5 0.5 0) and (3.5 0.5 0). However the integer Bragg peaks were unaffected in position or width by the application of the magnetic field. This magnetic effect will be described in detail in the next chapter. Such results are evidence that the charge density wave caused by the ordered disproportionation of bismuth atoms into non-equivalent Bi\textsuperscript{3+} and Bi\textsuperscript{5+} ions is incommensurate with the primitive cubic host lattice. This is presumably linked to the buckling of the BiO plane (in both the \textit{a*} and \textit{b*} directions) caused by the different coordination geometries of the two ions.

Scans through the CDW satellites along \textit{a*} demonstrated that they are elongated in the radial direction. Figure 6-4 shows the comparison of linear scans through a CDW satellite and a Bragg reflection. It is clear that the CDW satellite is anomalously broadened indicating that the CDW has a smaller correlation length. The curves drawn through the data points were fitted by a Gaussian function for the Bragg peak and a Lorentzian function for the CDW satellite. The best fits to the profiles gave peak widths (FWHM) of 0.0200\textdegree for the CDW satellites and 0.0125\textdegree for the Bragg reflections which accord with correlation lengths of ~150\textdegree and 250\textdegree respectively. Although the charge-density wave state is thought, in the case of BaBiO\textsubscript{3}, to be local having a very short coherence length (~ few \textdegree) of the order of the lattice parameters as estimated from the large optical gap of ~2 ev [122], such a localised CDW modulation could not be evidenced in this experiment due to the extreme broadening such a small
Figure 6.4. One dimensional scans along a* through the (2 0 0) Bragg reflection and the (1.494 0.011 0) CDW satellite at $T=295$ K showing the increased width of the CDW satellite.
correlation length.

Support for such observations can be found in the optical reflectivity measurements of BPBO by Tajima et al. [122] who found a CDW-induced pseudogap extending from the semiconducting to the metallic state. More recently, Boyce et al. [142] employed EXAFS spectroscopy to study the distortions around bismuth and lead atoms in BPBO and found results consistent with a local CDW in the metallic state. In the corresponding BKBO series, Karlow et al. [143] have observed the persistence of the IR absorption band into the metallic regime, which is again consistent with a local CDW. Furthermore a large peak in the optical conductivity has been observed to evolve from the CDW distortion in the composition range where superconductivity occurs [144]. Recent theoretical models also provide a basis for explaining these experimental results and their relevance to the superconducting mechanism in such materials. In the pioneering work of Rice and Sneddon [145] they interpreted the semiconducting behaviour of BaBiO₃ as due to real space electron pairing which gives rise to the valence configuration Ba₂Bi³⁺Bi⁵⁺O₆. Dilution weakens the intersite interaction and causes a phase transition to a metallic state which undergoes k-space (BCS) pairing at low temperatures. Later studies by Jurczek and Rice [146] included the modification required when the conduction band is broad as calculated by Mattheiss and Hamann [121]. Such an effect caused the formation of a local CDW. In subsequent theories, enhancement of Tc is predicted close to the semiconducting phase which is associated with the CDW [147].

Experiments were also conducted at low temperatures to study the effects of the metallic-superconductor phase transition. As noted in the previous study [141]
the CDW continues to exist at all temperatures down to 15K and therefore coexists with the superconducting state. Detailed measurements of the position and width of the CDW satellites failed to detect any variation with temperature and thus this incommensurate CDW exists in both the metallic and superconducting phases. However, as shown in Figure 6-5 the intensities of the CDW satellite were observed to have a pronounced variation with temperature. The intensity of the CDW satellites is related to the amplitude of the normal mode describing the structural distortion, $A_q$, through:

$$I_s(Q) = |F_s(Q)|^2 |A_q|^2$$

where $F_s(Q)$ is the structure factor of the satellite reflections and $|A_q|$ is related to the (half) gap

$$|\Delta_q| = g_q \sqrt{\frac{2\Omega_q}{\hbar N}} |A_q|$$

$\Delta_q$ in the band structure below $T_{CDW}[148]$. The results stated above show a marked decrease in integrated intensity of the CDW satellites with decreasing temperature [figure 6-6], in marked contrast to the increase in intensity of the associated Bragg reflections. Such behaviour is unusual, as in most CDW materials the satellites increase in intensity below $T_{CDW}$, relating the phase transition from the metallic state to the semiconducting state[151]. Such an unusual behaviour may indicate that the amplitude of the CDW distortion, $|\Delta_q|$, is decreasing with decreasing temperature because the magnitude of the pseudogap, $2\Delta_q$, decreases in both the metallic and superconducting phases. An estimate of the magnitude
Figure 6.5. One dimensional scans along \( a^* \) through the \((1.494 \ 0.011 \ 0)\) CDW satellite at \( T = 295 \) K, 99 K and 15 K. The solid lines are Lorentzian curves fitted to the data.
Figure 6.6. The variation of the integrated intensity of the CDW satellite with temperature. The solid line is a guide to eyes.
of the pseudogap can be obtained from the measurement of the correlation length, $\xi$,

$$\xi \approx \frac{\hbar \nu_F}{\pi \Delta_q},$$

with a Fermi velocity $\nu_F \approx 10^8$ cm/sec [121][152] and a measured correlation length of $0.02 \AA^{-1}$ being probably a lower limit as it is limited by the domain size, which suggests pseudogap energy of only $\sim 30$ meV. Such a small value may account for the inability of infrared reflectivity to distinguish the presence of a pseudogap in the metallic phase of BKBO [149] in contrast to that observed in BPBO where the pseudogap is much larger [122]. Hellman and Hartford deduced an energy gap of 46 meV in the normal state from the measurements of resistivity and Hall effect on BKBO epitaxial films [153] and they also suggested the presence of a metallic CDW. For BPBO the pseudogap decreases with increasing lead concentration which accounts for the formation of the metallic state above $x=0.65$. A similar decrease in the pseudogap would be expected to occur in BKBO close to the semiconducting to metallic (or superconducting) phase boundary. In the parent compound, BaBiO$_3$, the optical gap ($\sim 2$ eV) is due to the formation of a CDW state consistent with the splitting of the bismuth (6s) band which is not significantly reduced by lead substitutions throughout the semiconducting region; upon further doping the appearance of the metallic phase is due to the slight overlap of the bismuth (6s) bands [figure 6-7], suggesting the formation of a pseudogap in the metallic state[161][158]. However, substitutions of potassium on barium sites have somewhat similar effect on the electronic structure near the
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Figure 6.7. Schematic representation of the electronic structure of BaPb$_{1-x}$Bi$_x$O$_3$ near the Fermi level [158].
Fermi level. As the conduction band consists mainly of bismuth (6s) and oxygen (2p) states, the alloying with lead on bismuth sites or potassium on barium sites enhances the hybridisation of this conduction band leading to the pseudogap behaviour [159] [160], and further increases the singularity of the density of states (DOS) at the band edge [150][123]. Qualitatively, a higher DOS has been found in $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ ($T_c \sim 30 \text{ K}$) than that in $\text{BaPb}_{0.65}\text{Bi}_{0.35}\text{O}_3$ ($T_c \sim 12.5 \text{ K}$) [162][158], whereas the substitutional lead doping on the active bismuth sites has a stronger effect on the Bi(6s)-O(2p) conduction bands. Since the substituted lead atoms remain tetravalent having one less electron than bismuth, the lead substitution does not supply the Bi-O network with extra holes. Although alloying with lead can restore the destroyed Fermi surface, it may be responsible for the decrease of the DOS when the substitution is beyond the critical value. In contrast to the case of BPBO, the dopant potassium on the inactive barium sites only has a minimal effect on the electronic states near the Fermi energy, and extends the metallic regime of these alloys closer to half filling [121]. This therefore causes a distortion of the CDW leading to an imperfectly nested CDW at the Fermi surface.

6.4 Summary and Conclusions

The crystal structure of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ has been reported by Schneemeyer [119]. Single crystals of the superconducting composition $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ were found to be simple cubic with only one Bi site, suggesting no bond charge disproportionation is present and therefore no CDW modulation exists as well. In the present
work an incommensurate superstructure induced by the formation of charge-density waves has been identified using x-ray scattering in the superconductor Ba$_{0.6}$K$_{0.4}$BiO$_3$, which is an indication of a charge disproportionational distortion on Bi sites as predicted by the band structure calculation [121]. Based on the finding of a CDW superstructure, the possible distorted crystal structure could be constructed as shown in figure 6-8, where only the breathing-mode distortion is present. Given the uncertainty in the profile and the position of modulated satellites due to their weak intensity, changes in both parameters as a function of temperature can still not be exactly determined. Such work is necessary to further investigate using a synchrotron radiation source.

As known in some CDW materials the incommensurate CDW, as observed in NbSe$_3$ in both CDW states, can be easily depinned from impurities which enhances the conductivity due to the sliding CDW when the applied electric field exceeds the threshold value. None of the reports reveal the existence of a sliding CDW transport behaviour in this BKBO system so far, but it may be due to the quite weak pinning strength existing between the CDW and impurities. Such a behaviour should be detectable by x-ray scattering measurements with applied electric fields, because the profile of the CDW satellites could be broadened by the application of an electric field exceeding the threshold field [91][92]. A noticeable feature in this experiment is the decrease in the intensity of CDW reflections as temperatures lowered. The integrated intensity of the CDW peak is related to the amplitude of the normal mode which is responsible for the gap opened at the Fermi surface. This gap has been confirmed in the starting compound BaBiO$_3$, and a pseudogap in the metallic phase of the BPBO compound [122]. Further a pseudogap in the metallic state of the BKBO has also been reported.
Figure 6.8. A breathing-mode distorted structure of Ba$_{0.6}$K$_{0.4}$BiO$_3$. Blue balls show the positions of the mixture of (Ba+K), and Oxygen atoms are at each corners of the octahedrons (some of them are shown in red). Two non-equivalent Bi$^{3+}$ and Bi$^{5+}$ occupy the centers of octahedrons in turn, resulting in two different sizes of octahedrons as shown in yellow and brown.
in some optical spectrum measurements. Based on the hypothesis of the competition between the superconductivity and the CDW distortion, a decrease in the amplitude of the CDW distortion is plausible as the superconductivity emerges.
Chapter 7

A metastable CDW state in the superconductor \( \text{Ba}_{1-x}\text{K}_x\text{BiO}_3 \)

7.1 Introduction

As discussed in the previous chapters the Fermi surface instabilities due to the formation of a charge-density wave (CDW) or a spin-density wave (SDW) can lead to a variety of collective states in the low-dimensional materials and even in the high \( T_c \) perovskite superconductors \( \text{Ba}_{1-x}\text{K}_x\text{BiO}_3 \) and \( \text{BaPb}_x\text{Bi}_{1-x}\text{O}_3 \). Some of these distortions completely destroy the Fermi surface, and then leave a semiconducting state, but under some circumstances an incommensurate modulation with an imperfectly nested Fermi level can enhance the conductivity. One of questions based on the structural information is what will happen when such a material is exposed to an external magnetic field. A fascinating aspect of this question is the quantum oscillations resulting from the modification of the Fermi surface being divided into many subgaps opening at the zone boundaries of the
superlattice of the density wave (DW), which makes such a phenomenon observable using x-ray or neutron scattering, if the beam intensity is sufficiently high.

A growing number of articles have been devoted to discuss the properties of the electron gas system under the presence of a magnetic field. Experimentally, these have usually been restricted to the unusual transport behaviour, whilst there are almost no experimental observations of the change in the modulated structure under the influence of an applied magnetic field. Using x-ray scattering with an applied magnetic field of nearly 0.8 T, the CDW modulated structure has been observed to markedly change and with a very long relaxation time after the field was removed, this is characteristic of a metastable CDW state.

7.2 CDW instabilities in a magnetic field

The quantization of an electron gas has long been a topic of considerable interest in solid state physics. As is well known, an electron system exposed to a magnetic field polarizing the spin directions of electrons results in the Landau quantization of the energy spectrum, in which the density of states for motions perpendicular to the field will attain a discrete structure, the so-called Landau levels. If the field is strong enough, only one spin direction of the lowest Landau level will be occupied and associated with the motion parallel to the field. With this condition the energy spectrum will be characteristic of the one-dimensional conductors, while the simultaneous occurrence of a CDW state is predicted because in charge-density waves the two spin states are modulated in phase. The anomalous transport behaviours due to the magnetic-field-induced phase transition have been observed in a great number of experiments on heterostructures [165][166],
ABX$_3$-type antiferromagnets [167] and the graphite intercalates [168][169]. The presence of a superlattice is characteristic of such a field-induced phase, and some of them have been ascribed to the formation of a CDW modulation.

Within the presence of an applied magnetic field the kinetic energy of electrons perpendicular to the field is quenched, so that the dispersion is one dimensional and this results in a perfectly nested Fermi surface. Such a distorted ground state of the electron gas system therefore has a lower translational symmetry than the original crystal structure. This broken symmetry is also reflected in the changes of order parameters through a divergent susceptibility $\chi(q)$ [176]

$$\chi(q) = \sum_k \frac{f_k - f_{k+q}}{\varepsilon_{k+q} - \varepsilon_k}$$

at the modulated wavevector which may be incommensurate or commensurate with the host lattice, where $f_k$ is the Fermi-Dirac distribution function and $\varepsilon_k$ is the energy at the state $k$. Such a non-zero susceptibility has a dependence on the nesting condition of the Fermi surface. It is also worthwhile to note that the two kinds of broken symmetry states caused by the charge-density wave (CDW) and the spin-density wave (SDW) are fundamentally different. CDW's are caused predominantly by the electron-phonon interaction and produce a charge redistribution throughout the crystal, whereas SDW's are induced by the repulsive electron-electron interaction and produce a spatially varying spin polarization. However when both systems are exposed to a magnetic field they have a similar effect on their electronic structure [163].
Recently there has been much attention given to the interaction and the effect of an applied magnetic field on density wave (charge-density waves and spin-density waves) systems [177] [178] [179]. Calculations demonstrate that the presence of a high magnetic field in certain directions of CDW or SDW materials having imperfect nesting at the Fermi surface destroys these electron and hole pockets, opening a gap in the electronic spectrum at the Fermi level, and leads to a metal-insulator transition. This effect has been observed in the CDW and SDW materials such as the NbSe$_3$ [180], and the organic compounds (TMTSF)$_2$PF$_6$ [194] and (TMTSF)$_2$ClO$_4$ [193].

### 7.2.1 Magnetic effects on the CDW material NbSe$_3$

Niobium triselenide (NbSe$_3$) is the most extensively studied material in investigations of unusual phenomena caused by the charge-density wave (CDW) and exhibits two independent CDW transitions, one with an onset temperature $T_1=144$K and the other one with transition temperature $T_2=59$K. The latter arises from the only partially nested Fermi surface leading to the existence of electron and hole pockets which are responsible for the semimetallic conductivity. Owing to this partially destroyed Fermi surface, the second CDW causes the anomalous collective state when the material is exposed to an external field such as the presence of the superconductivity under high pressures, the sliding CDW under an electric field exceeding the threshold value and anomalous magnetotransport under an external magnetic field.

A typical feature of the magnetic-field-induced effects in the CDW state can be observed on the anomalous enhancement in the resistance [figure 7-1]. When a
pure NbSe$_3$ single crystal is oriented with the chain direction perpendicular to an applied magnetic field, a very large magnetoresistance is observed in the temperature range 10<$T<$50K for the applied electric field not exceeding the threshold value, and this increase declines very rapidly as the temperature approaches 59K ($T_2$). This additional resistance has been shown to be enhanced through an improvement of the nesting condition at the Fermi surface, and therefore leading to an increased gap and the conversion of carriers from the normal state to the CDW state. Using a two fluid model Ong and Monceau [38] inferred that the decrease in the resistance due to the sliding CDW originates from the conversion between the normal carriers and the CDW carriers, which also indicates the Fermi surface decreases by 60% as compared with that at the $T_1$. On the other hand, the enhancement in the magnetoresistance has also been interpreted as caused by a reduction of the Fermi surface area, which further indicates that most of the Fermi surface (~92%) must be destroyed at $H$=22.7T [180]. This would imply an enhancement in CDW carrier concentrations due to the application of a field strength of 22.7T.

It is clear in figure 7-1 that the temperature of the maximum resistance has been changed from ~50K to ~35K under the presence of a magnetic field strength of 9.6T. Shifts in this maximum under the condition of an applied magnetic field have been shown to be due to the enhancement in the fluctuations coming from phases of the CDW condensate because the magnetic field reduces the freedom of the spins of the CDW condensate [175]. The transition temperature is essentially unchanged in a transverse magnetic field of 9.6T. A theoretical model proposed by Balseiro and Falicov [163] predicts that the transition temperature for a CDW having an imperfectly nested Fermi surface may be increased in the presence of a
Figure 7.1. The magnetic effect on the resistance for the CDW material NbSe₃. The magnetic field enhances the resistivity below the CDW transition temperature $T_2=$59 K, whilst $T_2$ remains essentially unchanged [164].
high magnetic field. However, this increase in the CDW transition temperature has been observed in a higher magnetic field in which the $T_c$ was increased by 0.5K in a field strength of 22.6T [175], this finding also supports the Balsiro-Falicov model.

When the applied electric field exceeds the threshold value, the magnetoresistance $R(H)$ appears to be independent of the magnetic field. Without the application of magnetic field the charge-density waves start to move and the resistance drops rapidly when the electric fields exceed the CDW depinning field. The rapid decrease in resistance at higher electric fields is associated with the extra current being carried by the moving CDW. In the presence of a magnetic field the extra magnetroesistance also decreases rapidly as the electric field increases above the threshold value as shown in figure 7-2. At sufficiently high electric fields the resistance approaches that observed at $H=0$. This magnetoresistance being quenched at high electric fields is due mainly to the sliding CDW state.

The collective transport behaviour of the CDW condensate is dominated by the mutual interaction between the kinetic energy and the phase of the CDW state. With an applied magnetic field the motion of electrons are restrained in directions perpendicular to the magnetic field, in such a way that the energy of the CDW condensate associated with spatial distortion of the phase, or the kinetic energy associated with the phase fluctuation, is reduced [178]. Such a reduction may also play a dominant role in depinning the CDW from impurities, i.e. the pinning energy needed to overcome the sliding CDW is less than that without the presence of an applied magnetic field, because the threshold electric field for the sliding CDW state has been reduced when an external magnetic field is applied. From the measurements by Monceau et al. [181] the threshold
Figure 7.2. The resistance of NbSe$_3$ at 30 K as a function of an applied electric field, measured at H=0 (open circles) and H=22.7 T (solid circles) [180].
electric field was observed to change from \( \sim 0.75 \text{V/cm} \) at \( H=0 \) to \( \sim 0.2 \text{V/cm} \) at \( H=20 \text{T} \) at \( T=1.8 \text{K} \). Owing to this field-induced localization of electrons of the CDW condensate, the anisotropic properties in the correlation length has been ascribed to the phason propagating along the transverse direction \([178]\), because of the smaller effects on the longitudinal correlation length.

The magnetoresistance observed in \( \text{NbSe}_3 \) below the second CDW \( (T_2=59 \text{K}) \) is dependent on the angle between the magnetic field and the transverse orientation. For the field parallel to the chain direction the magnetoresistance decreases by a smaller amount as shown in figure 7-3. Such a dependence is linked to an unusual modification of the Fermi surface induced by the CDW. In this quasi-one-dimensional material the Fermi surface is composed of nearly planar sheets (a nested Fermi surface) oriented perpendicular to the chain direction, therefore an applied magnetic field has a maximum effect on the Fermi surface if the field is oriented perpendicular to the chain direction. None of the magnetoresistance enhancement is observed at temperatures above 59K, where only the higher temperature CDW destroying most the Fermi surface sheets is present, so there is a strong indication that the imperfect nesting effects on the Fermi surface sheets play a critical role in the required mechanism.

### 7.2.2 Metastable CDW states

There have been considerable efforts devoted to investigating the unusual dynamic and static phenomena in materials having such a charge-density wave modulation. In addition to the aforementioned unusual behaviour, another character of CDW materials is the metastable state which is described in terms of
Figure 7.3. The magnetoresistance induced by transverse magnetic fields decreases smoothly as the field is rotated into a longitudinal orientation [175].
the time dependence and the field dependence. This slow relaxation phenomenon is also a characteristic of spin-glass behaviour. A reasonable physical picture of metastable states in the spin-glasses can be described as the spins of cluster, a nucleus together with its surrounding neighbours, and the surrounding of these spins being readjusted in order to reach a new energy minimum state which is also relative to the number of metastable states [182]. Such a conceptual understanding of the rearrangement of spins is compatible with that of the CDW metastable state.

In quasi-low-dimensional Peierls-Fröhlich systems, like NbSe₃, TaS₃, or blue bronzes, most of the scientific interests arises from the anomalous behaviour caused by the sliding charge-density waves appearing above an unusually low threshold field, in general in the range of a few mv/cm to a few hundred mv/cm. One of the remarkable manifestations of moving charge-density waves is the pulse-sign memory effect which occurs under the condition of an applied current or voltage pulses of alternating sign in a CDW material and reflects on the transient voltage oscillations [189]. Such a memory effect is due to the presence of metastable states of CDW. There are many different pieces of experimental evidence for the existence of metastable states in the density-wave (DW) systems, including both charge-density waves and spin-density waves, in the whole temperature range between their phase transition down to the lowest temperature. In materials having CDW modulations the metastable states are local fluctuations in the phase of the CDW because the impurities pinning on the CDW is inhomogeneous on a microscopic scale [187] [188].

By means of observations of the voltage- or frequency-dependent conductivity many researchers [183] [184] [186] [185] have also shown a weak relaxation in the
form of log \( t \). One of the common features is as shown in figure 7-4, where the data can be fitted with a logarithmic correlation between the relaxation times and the conductivity. This figure not only provides the time dependence of conductivity, \( \Delta \rho/\rho \), but also shows the temperature dependence of the relaxation rate.

Analogous to the random spin configuration in the glassy system the randomness of the pinning centers is also a key point in understanding the long time-scale relaxation, indicating that the physical properties in the CDW system are strongly affected by the rearrangement of pinned CDW configurations [184].

At higher temperatures, the mean value of the relaxation-time distribution is thermally activated, involving the screening of the CDW deformation by normal carriers. This prevents, somewhat, the metastable CDW state from being observed at higher temperatures due to a too short relaxation process. But this process will be extended to a longer period due to the limited thermal excitation at lower temperatures. To measure the energy relaxation in the CDW materials, \( \text{TaS}_3 \) and \( \text{NbSe}_3 \), below \( T=0.5 \) K and without application of any electric field and magnetic field, Biljakovic and co-workers observed a long-time energy relaxation which increased as the temperatures decreased [190]. They ascribed this effect to the deformation in the internal freedom of the CDW condensate.

In a model described by Lee and Rice [191] the CDW phase coherence was assumed to be long in all directions. If the pinning was only due to homogeneously distributed impurities and the applied field was also homogeneous, the CDW would depin at a threshold field simultaneously in the whole crystal. If, however, the field and/or the pinning forces are inhomogeneous a partial depinning may be more favourable. This partial depinning process is responsible for the long-time relaxation observed in voltage- or frequency-dependent conductivity. The above
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Figure 7.4. Time dependence of conductivity $\rho$ after switching off the field and at different temperatures on a single crystal of TaS$_3$. $\Delta \rho = \rho(t) - \rho_0$, where $\rho_0$ is measured at the electric field exceeding the threshold value. Decrease of $\Delta \rho$ corresponds to the spontaneous decay of metastable states [183].
Figure 7.5. Schematic pictures of pinning effects coming from a.) homogeneous impurities and b.) inhomogeneous impurities. The large solid arrows indicate the ground state, and open arrows present metastable states.
descriptions can be schematized simply as shown in figure 7-5. Considering the application of an electric field exceeding the threshold value in a CDW material, assuming that the pinning potential produced by homogeneous impurities is also uniform throughout the whole lattice, this configuration will result in a sliding CDW. However, if the applied electric field is lower than that needed for exceeding the potential the CDW would tend to stay in the ground state as the stable state. On the other hand, if impurities are randomly distributed they will cause the pinning of the CDW to be non-uniform. Under such circumstances the CDW will take a long time to relax to the ground state after the field (E>E_T) has been switched off, because of the presence of pseudo-stable states (metastable states). Generally speaking the initial metastable state is always far from the lowest energy state (ground state), an increase of the electric field will allow the phase of CDW condensate to continuously deform to minimize the energy gain from the electric field. At low field, the CDW remains within a single valley of the potential, but as the field is increased further, local pieces of the CDW run over into the next well. This process continues to result in the sliding CDW when the field approaches or exceeds the critical value. If the electric field is switched off suddenly, the phase is frozen on the long length scale characteristic of the sliding state at that particular field, because of the presence of different potential wells, and keeps fluctuating with the decreased energy, which indicates that the CDW does not relax back to the initial configuration, but rather into a nearly metastable state. Consequently, the system will have to take a long time, depending on the details of the distribution of pinning strengths, for the CDW condensates to return to the equilibrium state [192].
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The Ba_{1-x}K_xBiO_3 system is a new member of materials exhibiting a charge-density wave distortion. From previous studies a superstructure has been observed in this material, but it is difficult to discern the nature of the distortion inducing such a modulated structure only from x-ray scattering. Based on the common characters of the CDW distortion, pronounced effects caused by an applied magnetic field as stated above, the application of magnetic field should have a marked influence on superlattice reflections observed in Ba_{0.6}K_{0.4}BiO_3, reflecting on the intensity and the profile of reflections, even a metastable CDW state. That is the motivation of the experiment described below.

7.3 Experiment

The sample used in this experiment was the same as that used in our previous studies [141][171], which has a on-set transition temperature at T_c~30K corresponding to x~0.4. The sample was mounted on a two-circle triple-axis diffractometer operating on a high brilliance rotating anode x-ray source. Monochromatic CuKα beams were selected and collimated using flat graphite (0001) monochromator and analyser crystals. Such a configuration gives a relatively poor resolution (~0.6° FWHM for the (3 0 0) Bragg peak), but very high intensities. Five Nd-Fe-B magnets were spaced by the sample in a gap of 4mm providing a field strength of nearly 0.8T. Such an arrangement is displayed in figure 7-6.
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7.4 Results and Discussion

Information about the modulated structure obtained from x-ray scattering does not demonstrate the nature of the modulation. The attribution of the weak supercell reflections to a CDW is supported by further measurements under a magnetic field. Measurements were conducted to observe the evolution of the modulated satellites under both conditions of the presence of an applied magnetic field with a strength of ~0.8T and a zero field. With a graphite monochromator and analyzer the modulated satellites can be located around the half-integer positions [141] which are single satellites as shown in chapter 4. Such results dramatically changed when the sample was exposed to a magnetic field strength of nearly 0.8T. As displayed in figure 7-7 the single satellite (figure 7-7a) can be resolved into two satellites at (3.49 - 0.012 0) and (3.49 - 0.044 0) (figures 7-7b and 7-7c) with a splitting of ~0.032 along the <010> b* direction.

Figure 7.6. Schematic representation of the experimental arrangement.
Figure 7.7. Isointensity contour plots of the x-ray scattering intensity around the CDW satellites close to \((3.5 \ 0 \ 0)\). A) Under ambient conditions. B) Under an applied magnetic field of 0.8T. C) after 6 days with the magnetic field on. D) 3 days after the magnetic field was removed. E) 30 days after the magnetic field was removed. The contour levels (counts per 30 seconds) from range 60 to 120 counts.
Higher resolution x-ray scattering measurements were performed utilizing a perfect Ge(111) single crystal and a detector receiving slit of width ~1.9mm. The CDW satellites were found to be composed of two peaks symmetrically displaced from integer Bragg positions by 0.494a* and ±0.011b* [171]. However, with the application of a magnetic field with a strength of ~0.8T the splittings along the <010> increased from 0.022 reciprocal lattice units to 0.032 r.l.u.. Zhang and co-workers also observed a similar splitting of the CDW satellite in K_{0.3}MoO_3 [91]. They performed x-ray scattering measurements with an applied electric field exceeding the critical field along the chain direction, and then observed the splitting in a direction perpendicular to the chain direction. This situation was ascribed to the splitting of the CDW domains.

After six days in the presence of the magnetic field, the splitting was still existent (figure 7-7c), until the field was removed and then it gradually decreased over a long period of time (from figures 7-7d and 7-7e). Linear scans through the satellite shown in figure 7-8 provide evidence that the satellite consisted of two peaks, one at (3.49 0.03 0) and the other at (3.484 0.002 0) as shown in figure 6-8. Attempts at exactly measuring the peak intensities and the peak widths failed, owing to the time-dependent nature of the transition, and the low peak intensities. Surprisingly, the CDW state did not relax to equilibrium configuration after the field was removed, but the splitting persisting for a prolonged period of ~30 days (figures 7-7d and 7-7e). Long-time relaxation phenomena are characteristic of metastable configurations of the charge-density waves [55]. Such a finding of a long relaxation process supports the evidence of a modulated CDW superstructure. Investigations using the x-ray scattering and large electric fields have shown the existence of a metastable state in K_{0.3}MoO_3 [195] [92], in
Figure 7.8. One-dimensional scans through the CDW satellite (3.5 0 0). Arrows indicate the scan directions during the relaxation process. Labels of the x-axis in a are the relative distance between both peaks along the scan direction a.
which the application of electric fields caused a broadening of the CDW peak width in directions both parallel and perpendicular to the chain direction, and the broadening remained unchanged after the field is removed.

The phenomena of separation and restoration of CDW satellites can not only be observed in the satellites around (3.5 0 0) but also in the satellites around (3.5 0.5 0) and (3.5 0.5 0) (figure 7-9). This anomalous behaviour induced by an applied magnetic field was only seen in satellites with a higher index, and this might suggest a tilting angle between the magnetic flux lines and the <100> direction and such a tilting angle therefore enhances the magnetic effect [170][177] on these high index CDW satellites. Such an explanation would explain why we could not find the separation around the (1.5 0 0) satellite. However, in further measurements taken on the BPEX diffractometer with a new holder for the magnets, so that the field could be rotated in a small range (~0 to 20 degrees around the sample), the splitting in the CDW satellite (2.5 0 0) appeared as shown in figure 7-10. The splitting in figure 7-10 gave an estimated value of 0.014 r.l.u. along the <010> direction, which is smaller than that observed in figure 7-7, indicating a strength dependence of the field-induced splitting. Taking the phase slip into account for the split of CDW domains, the phase difference between neighbouring domains is gradually changed under an applied magnetic field. Such a change may result from the driving force produced by impurities stirred by the external magnetic field.

As mentioned above the unusual magnetotransport behaviour of in NbSe$_3$ can be explained as carriers converting between the CDW condensate and the normal state. Within this framework, the intensity of CDW superlattice reflections would be expected to increase as the field strength increases. There are some remaining
Figure 7.9. Isointensity contour plots obtained from CDW satellites (3.5 -0.5 0) and (3.5 0.5 0) respectively under conditions of A) 8 days after the field was removed. B) 22 days after the field was removed. C) 30 days after the field was removed.
Figure 7.10. Isointensity contour plot of the CDW satellite $(2.5 \, 0 \, 0)$ under a magnetic field $0.6$ T with the sample with a tilted at an angle of $15^\circ$. 
unexplained results from this study. No splitting could be found in the CDW satellite (1.5 0 0) during both experiments mentioned above, so this CDW reflection was chosen to observe the magnetic effect on the CDW condensate. Data were collected under different field strengths parallel to the sample. As displayed in figure 7-11, the Bragg peak (2 0 0) is not influenced by the magnetic field up to 0.8 T, but there are significant changes in the intensity and the profile of the CDW peak at 0.8 T. In figure 7-12 scans through the longitudinal direction of the CDW satellite at (1.5 0 0) show obviously that the intensity dropped at 0.8 T, while the peak width increased from 0.027 r.l.u. (reciprocal lattice unit) at zero field and 0.45 T to 0.035 r.l.u. at 0.8 T. This behaviour seems to indicate that the threshold field $M_T$ might be between 0.45 T and 0.8 T probably depending on the orientation of the field with respect to the sample. Scans were also measured along the transverse direction of the CDW peak, i.e. perpendicular to the magnetic field, at 3 different magnetic fields, $M=0$, 0.45 and 0.8T as shown in figure 7-13.

Changes in the peak-width perpendicular to the field direction were not observed, which might be limited by the experimental resolution. Data obtained from the CDW reflection are in agreement with the fitting function

$$I(k) = \frac{\Gamma}{(k - Q)^2 + \Gamma^2}$$

where $\Gamma$ gives the half-width of the CDW peak. The best fits to the peak width of the CDW profile are listed in table 6-1.

It is noticeable that $\Gamma_t$ was increased by the applied magnetic field with a strength of 0.8 T while $\Gamma_l$ remained unchanged. This anisotropic behaviour is
Figure 7.11. Linear scans along $a^*$ of the Bragg peak (2 0 0) axis parallel to the field direction at two different field strengths, 0 T and 0.8 T. The solid line was fitted to a Gaussian function with a FWHM of 0.024 rlu. at $M=0.8$ T.
Figure 7.12. With an applied magnetic field exceeding 0.8T the CDW reflection undergoes pronounced changes in the intensity and the peak width parallel to the field direction. The solid and dotted lines were fitted with a Lorentzian function.
Figure 7.13. Scans along $b^*$ of the CDW satellite at $(1.495 \ 0 \ 0)$ at different field strengths, 0 T, 0.45 T and 0.8 T. Although the peak width remains unchanged, there is a remarkable decrease in the peak intensity at 0.8 T.
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<td>$\Gamma_t$</td>
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Table 7.1. The half-width of the CDW peak measured along the longitudinal direction $\Gamma_l$ and the transverse direction $\Gamma_t$, and at M=0, 0.45 and 0.8 T. The fitting errors are within ±0.0005 rlu.

The other remarkable change in the presence of applied magnetic fields exceeding the threshold field is the decrease in the intensity of the CDW satellites. A reduction of the intensity of CDW reflections indicates the suppression of a gap opened by the CDW at the Fermi surface, since the intensity of the superlattice reflections is proportional to the amplitude of the CDW condensate. In a recent investigation on the magnetic field induced transition in a spin-Peierls system using high resolution x-ray diffraction with an applied magnetic field up to 12.5 T [196], V. Kiryukhin et al. also observed a decrease in the intensity of the superlattice reflections induced by a Peierls transition below the transition temperature. They ascribed this phenomenon to the reduction of the magnetic gap at the magnetic field induced transition. Although the CDW system undergoes a Peierls transition at the transition temperature $T_{CDW}$ which then opens a
gap at the Fermi surface, the origin of the gap is different in both systems [197] [198]. In the case of the spin-Peierls, the gap appears due to the singlet-triplet transition of a spin-$\frac{1}{2}$ antiferromagnetic chains at the transition temperature, but that is due the modulation of the electron density in the CDW state. A different explanation was given by Tritt and coworkers [164] after measurements of the magnetotransport in the CDW material NbSe$_3$. They explained that the enhancement of the resistance as shown in figure 7-1 is due to an increase of the CDW carrier concentration. If this hypothesis is right, then that should imply an increase in the intensity of the superlattice reflections. However, this conflicts with our findings. This discrepancy may result from the dimensionality. Conventional CDW materials possess an anisotropic energy gap such that the conductivity is enhanced in the specific directions. Our sample, Ba$_{0.6}$K$_{0.4}$BiO$_3$, is cubic and has an isotropic conductivity, so electrons have more degrees of freedom in which to move. Further study, both theoretical and experimental, is clearly needed to adequately explain such phenomena.

7.5 Summary and conclusions

In this study, some unusual and interesting phenomena have been observed in the superconductor Ba$_{0.6}$K$_{0.4}$BiO$_3$ under condition of an applied magnetic field up to 0.8 T, and are summarized as follows,

1. A metastable CDW state was observed.

2. The structure of CDW domains can be influenced by an applied magnetic field exceeding the threshold strength.
3. The magnetic field induces an anisotropic behaviour on the ordering of the CDW.

4. The intensity of the CDW superlattice reflection is decreased when the field strength is increased.

As is well known, the transport properties of CDW materials are dramatically affected by magnetic fields which is ascribed to the destruction of small electron and hole pockets leading to a better effective nesting of the Fermi surface, further causing the decrease of current carriers of the normal state. Investigations of the anomalous magnetoresistance behaviour have ascribed that this unusual phenomenon to a change in the charge-density wave concentration rather than any dynamical motion of the CDW. However, this study has shown that the magnetic field not only changes the carrier densities of the CDW condensate, but also changes the order parameter of the CDW wavevector. Such a change is possible if the magnetic field constrains the motion of electrons to the direction perpendicular to the field direction, and then causes the rearrangement of the CDW condensate in order to reduce the energy gain from moving electrons. Such a behaviour may cause an increase of the phase difference between domains due to inhomogeneous strains induced by the magnetic field on domains, which then further enhances the splitting of CDW satellites. Owing to the presence of potential walls produced by impurities positioned at random, this system needs a long period to relax to the equilibrium state when the field is removed. It is also noteworthy that the ratio of $\Gamma_1/\Gamma_1$ increases at $M=0.8$ T, indicating an enhancement of the fluctuation along the longitudinal direction. Fluctuation effects in conventional CDW materials approaching the critical temperature can
lead to pronounced changes in the density of states, and thus result in a gradual opening of the pseudogap. In a recent study by Bjeliš and Maki [199], they considered a magnetic field perpendicular to the most conductive plane in quasi-two-dimensional CDW materials and constructed a model indicating that the magnetic field has no influence on the longitudinal correlation length but causes a decrease in the transverse length as the field is increased. This then enhances the fluctuation-induced specific heat and the resistivity in the chain directions. Our findings from $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$, which possesses an isotropic transport behaviour in the 3-dimensional structure, are at variance with their theoretical model.

Although the modulated superstructure has been confirmed to be induced by the formation of a charge-density wave distortion, there still remain some questions which are necessary for understanding the transport properties. One of these questions is what is the nesting condition of the Fermi surface? As in most CDW materials an imperfectly nested Fermi surface contributes to a higher conductivity below $T_{\text{CDW}}$, and BKBO is expected to have an imperfectly nested Fermi surface because of the properties of the good conductivity at room temperature and a high superconducting transition temperature. The demonstration of this speculation will rely upon the investigation of the photoemission measurements or de Haas-van Alphen experiments. It is also important to investigate the coupling between the superconducting state and the CDW state. Using the Raman scattering with an applied magnetic field, Sooryakumar et al. [84] observed the coupling between both states in $2H$-NbSe$_2$ as mentioned in chapter 3. However, these unusual phenomena still need to be studied further in order to understand the role played by the CDW condensate in collective effects in this high-$T_c$ copper-free superconductor.
Chapter 8

Conclusions and Further Work

8.1 Conclusions

Using x-ray scattering on a variety of single crystals of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, a modulated structure was observed in all samples measured including superconducting and semiconducting compositions, which was ascribed due to the formation of a CDW modulation. A series of experiments were designed to study the temperatural effects and the magnetic effects on this modulated superstructure. In the low temperature measurements, data shown a coexistence of the superconducting state and the CDW state. With the application of a magnetic field at room temperature, the CDW satellites displayed various unusual phenomena. The preliminary results described in this thesis can be summarized as follows:

1: Low resolution measurements

Two flat pyrolytic graphite crystals were used to select the $\text{CuK}_\alpha$ x-ray beam
produced from a high-brilliance rotating anode generator operated at 2.7 kW with a Cu anode and collect the scattered x-ray beam from the sample. Such a configuration provided a resolution of $\sim 0.01 \text{ Å}^{-1}$. Data obtained from a superconducting sample which has a superconducting transition temperature of $T_c \sim 30 \text{ K}$ corresponding to a composition of Ba$_{0.6}$K$_{0.4}$BiO$_3$ show satellites positioned around $(h k 0)$ half-integer positions as shown in Figure 5-8. Linear scans through these satellites demonstrated that they are the superlattice reflections enlarging the unit cell. The similar results were also observed from other samples grown by other groups. This larger supercell was ascribed to the presence of a charge-density wave caused by the ordered disproportionation between non-equivalent Bi$^{3+}$ and Bi$^{5+}$ ions. These satellites were observed to persist down to 15 K, indicating the coexistence of both superconducting state and CDW state.

Comparison was also made to a semiconducting crystal measured at room temperature. Overall they showed considerable similarity. Superlattice reflections were also observed to surround the $(3 0 0)$ Bragg peak at half-integer positions along the $[1 0 0]$, $[0 1 0]$ and $[1 1 0]$ directions in the semiconducting sample. The major difference between the two compositions was found by a scan in the $[1 0 0]$ direction (see figure 5-14). Additional peaks were located at $(1.67 0 0)$, $(2.67 0 0)$ and $(3.67 0 0)$, which are not present in the metallic or superconducting state. Scans through the transverse and the longitudinal directions of $(3.67 0 0)$ gave an estimated ratio of correlation length, $\varepsilon_{\parallel}/\varepsilon_{\perp} \sim 2.2$.

2: Intermediate resolution measurements
In this experiment, a perfect Ge(111) single crystal and a detector receiving slit of width \( \sim 1.9\text{mm} \) were used to monochromate and collimate the incident CuK\(_{\alpha 1}\) and scattered beams, respectively. Such an arrangement provides an instrumental resolution of \( 10^{-3}\text{Å} \), and only allows scattered X-rays to reach the detector if they have both the correct wavelength and scattering angle. Under such a resolution, the satellites observed by low resolution measurements around the half-integer positions were resolved to be composed of two peaks symmetrically displaced from the [100] axis as shown in figure 6-2. The positions of the CDW satellites are therefore to be displaced from integer Bragg peaks by \( 0.492a^* \) and \( \pm 0.011b^* \);

\[
\vec{q}_{\text{CDW}} = 0.492a^* \pm 0.011b^*.
\]

Scans through the CDW satellites demonstrate that they are broadened relative to neighbouring Bragg reflections, and their inverse correlation length was obtained to be \( 0.02\text{Å}^{-1} \) from the fitted Lorentzian curve.

Experiments were also conducted at low temperatures to study the effects of the metallic-superconductor phase transition. Detailed measurements of the position and width of the CDW satellites have failed to detect any variation with temperature and thus the incommensurate CDW exists in both metallic and superconducting phases. However, as shown in Figures 6-5 and 6-6 the intensities of the CDW satellite were observed to show a pronounced decrease with decreasing temperatures, in marked contrast to the increase in the intensity of the associated Bragg reflections. Such an unusual behaviour may indicate a decrease of the band gap induced by the formation of the CDW state as temperatures decreased.
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3: Low resolution measurements with the application of the magnetic field

The attribution of the weak supercell reflections to a CDW is supported by further measurements under a magnetic field. Five Nd-Fe-B permanent magnets were used to provide a magnetic field of nearly 0.8 T. The experimental arrangement was identical to that employed in the low resolution measurements. With such a low resolution the CDW satellites cannot be resolved, but the application of a magnetic field of ~0.8 T results in a dramatic increase of the splitting from 0.022b* measured by the intermediate resolution measurements to 0.032b*. This splitting persisted when the field was removed and gradually decreased over a long period of time. The splitting returned to its ambient value only after a prolonged period of ~30 days (see Figure 7-7).

With further studies of this magnetic effect on the CDW satellites, we found that the modification of the CDW modulation depends not only on the field strength but also on the orientation of the field with respect to the sample. By rotating the magnets a small angle (~15°) with respect to the sample, the satellite (2.5 0 0) split similar to that found around the (3.5 0 0), but with a smaller splitting (see Figure 7-10). However, the (1.5 0 0) satellite was not observed to split during the measurements with an applied magnetic field, so it was chosen to observe the evolution of the CDW profile with the field strength. The profile of nearby Bragg peaks such as the (2 0 0) reflection did not change up to 0.8 T as shown in Figure 7-11, but the intensity of the CDW satellite reflection changed markedly as the field strength was increased up to 0.8 T as shown in Figure 7-12 and 7-13. While the peak width of the CDW satellite reflection increased only
along the longitudinal direction, indicating a shorter range order caused by the applied magnetic field exceeding a critical field along the longitudinal direction.

8.2 Further Work

Modulated satellites have been observed in the high-$T_c$ superconductor $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ using the rotating-anode x-ray source, and were suggested to be due to the formation of a charge-density wave state, but many questions remain unclear, for instance, whether the CDW modulation in the metallic or superconducting state is a localised CDW state as that reported by Rice et al. or a long range ordered CDW? and whether the metallic CDW state is really suppressed at the low temperatures? or even the question; do the modulated satellite reflections observed really originate from the formation of a charge-density wave state? In the neutron and electron powder diffraction measurements, a composition (concentration of K) dependence of the CDW wavevector was also reported. This dependence is one of the key points for understanding the conductivity in this BKBO compound. All these unanswered questions in this thesis are mainly limited by the weak intensity of the satellite reflections and the availability of the higher quality single crystals with different concentrations of potassium. It is necessary to repeat these measurements for the semiconducting composition and also at low temperatures where BKBO is superconducting using synchrotron x-ray scattering on the higher quality single crystals. These experiments will demonstrate the relationship between the CDW and the superconducting properties of BKBO across the composition range.
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The sensitivity of x-ray to lattice modulations, and the availability of high resolution and high-brilliance from synchrotron radiation have therefore provided a powerful probe for the detailed study of the modulated structures; both superiorities enable the observed reflections only to be from a single domain of a crystal sample. After finishing this thesis, similar results but from more precise measurements were obtained at room temperature on a superconducting sample using synchrotron x-ray scattering at Daresbury Laboratory.

The superconductivity observed in the classic CDW material NbSe$_3$ under high pressure is ascribed to the restoration of the Fermi surface. The imperfect nesting Fermi surface has been believed to play a crucial role in the coexistence of superconductivity and charge-density waves. Although an incommensurate CDW has been observed to coexist with superconductivity in BKBO, it is still unclear what the nesting condition is in the superconducting state. As contrast with the application of high pressure, an applied magnetic field was believed to enhance the CDW carrier density, then resulting in an enhancement of the resistivity. By applying a magnetic field of $\sim 0.8$ T to a superconductor of BKBO, the intensity of the superlattice reflections was observed to decrease, which should indicate a decrease in the CDW carrier density as the field strength increased. Both results seem to conflict with each other. In order to further investigate both static and dynamic phenomena of the charge-density wave (CDW) with and without the application of external fields, a series of experiments using synchrotron x-ray scattering and neutron scattering have been scheduled and planned to be undertaken at Daresbury, NSLS (Brookhaven National Laboratory) and ESRF (European Synchrotron Radiation Facility).

It is also worth to review another similar compound BaPb$_{1-x}$Bi$_x$O$_3$ which has
been reported to have a pseudogap caused by a CDW state in the metallic state being a superconductor at \( \sim 12 \) K. As the conduction band consists mainly of Bi(6s) and O(2p) states, alloying with Pb on Bi sites enhances the hybridisation of the conduction band leading to the formation of a pseudogap and an increase of the density of states (DOS) at the band edge. Qualitatively, a higher DOS has been found in BKBO than in BPBO which may account for the higher \( T_c \). BPBO therefore offers a similar series as BKBO to investigate the formation of a CDW distortion. If the the incommensurate CDW distortion is caused by buckling of the Bi-O planes then substitution of the bismuth by lead should have a profound effect on the intensity and the width of the CDW satellites.

Although CDW-type distortions have been invoked to explain the semiconducting properties of BaBiO\(_3\) and the occurrence of superconductivity in the lead and potassium-doped series, it is only very recently that CDWs have been invoked in other superconducting materials. In La\(_{2-x}\)Ba\(_x\)CuO\(_4\) the superconducting temperature varies considerably with composition. In particular the superconducting phase disappears around \( x=0.125 \) which is believed to be due to the formation of a CDW. Another candidate for searching the CDW modulation relating to the superconductivity is the alkali fullerides \( A_3C_{60} \) (\( A=\) K, Rb and Cs). \( A_3C_{60} \) constitute a new class of high temperature superconductors with properties very different to those of the cuprates. Theoretical calculations using the Hubbard model have shown a CDW state semimetallic phase with a superconducting ground state. Despite this, the CDW state has not yet been directly observed, the calculations do provide values of the resistivity, coherence length and penetration depth in agreement with experiment. This therefore constitutes a new series of materials where CDWs may have important consequences. Among the
high-$T_c$ superconductors, a CDW modulation has been observed in the archetypal superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO-123) along the c-axis by reversed-bias STM measurements. Owing to the growing theoretical models and experimental findings, a CDW distortion may exist in these high-$T_c$ superconductors and contribute to their superconductivity. The observation of the CDW modulation using x-ray and neutron scattering is therefore important to help the understanding of any linkage between the CDW and superconductivity.
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