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1994 J. Phys.: Condens. Matter 6 L575

(http://iopscience.iop.org/0953-8984/6/39/001)

J. Phys.: Condens. Matter 6 (1994) L575–L581. Printed in the UK

LETTER TO THE EDITOR

Observation of a charge-density-wave-induced supercell in single-crystal $Ba_{1-x}K_xBiO_3$

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Received 18 July 1994, in final form 15 August 1994

Abstract. The structure of $Ba_{1-x}K_xBiO_3$ has been investigated by triple-crystal x-ray scattering on a variety of single crystals of different compositions. Attention has focused on the modulation observed by electron diffraction in the ⟨110⟩ directions. None of the incommensurate reflections observed in such studies have been observed with x-ray scattering, evidence that such observations are caused by electron-beam-induced damage. However, superlattice reflections have been observed at $(hk0)$ half-integer positions, evidence of a larger supercell due to the presence of a charge density wave caused by the ordered disproportionation between non-equivalent Bi(III) and Bi(V) ions. This commensurate modulation exists in both semiconducting ($x < 0.37$) and superconducting ($x > 0.37$) compositions.

$Ba_{1-x}K_xBiO_3$ exhibits the highest superconducting transition temperature ($T_c = 30$ K for $x = 0.4$) reported for any oxide not containing copper. The transition from an orthorhombic semiconductor ($x < 0.37$) to a cubic metallic or superconducting perovskite phase ($x > 0.37$) has enlivened great interest, as it might provide a clue to the superconducting mechanism. $Ba_{1-x}K_xBiO_3$ ($x > 0.37$) provides a model system for investigating superconductivity in oxides. The most striking structural feature of this material is its simple crystal structure, being primitive cubic ($Pm\bar{3}m$) down to at least 10 K [1]. Thus the material does not exhibit the two-dimensional metal–oxygen planes so prevalent in the copper-based ceramics which are widely believed to be an essential feature of high-T_c superconductors.

The parent compound $BaBiO_3$ is monoclinic ($I2/m$) [2] in which oxygen-breathing mode distortions cause a commensurate charge-density wave (CDW) giving an ordered arrangement of Bi(III) and Bi(V) ions. This commensurate CDW creates an insulating gap at the Fermi surface which accounts for the semiconducting behaviour of $BaBiO_3$. Recent research has focused on the interaction between CDWs and superconductivity in the substituted series $BaPb_{1-x}Bi_xO_3$ and $Ba_{1-x}K_xBiO_3$. The $BaPb_{1-x}Bi_xO_3$ system exhibits superconductivity with T_c varying from 0.45 K for $x = 0$ to 13 K for $x = 0.25$ [3]. Above $x = 0.30$, the system is semiconducting due to commensurate CDWs as in the parent material $BaBiO_3$. The importance of the relationship 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. Such a relationship has previously been demonstrated in the chevrel phases [4]. The relationship has been further advanced by optical reflectivity measurements by Tajima *et al* [5] who showed that the CDW energy gap exists as what they call a 'pseudogap' in the metallic region and that it changes smoothly with composition into a 'true' gap for $x > 0.3$.

0953-8984/94/390575+07$19.50

The behaviour of $Ba_{1-x}K_xBiO_3$ is similar to that of the $BaPb_{1-x}Bi_xO_3$ system and displays the expected correlation between CDWs and superconductivity. The motivation for studying $Ba_{1-x}K_xBiO_3$ was that a more appropriate doping might suppress the commensurate CDW and create a metallic (and superconducting) compound closer to the half-filled band condition of $BaBiO_3$. Such a compound might then exhibit a higher T_c because of the stronger electron–phonon interaction near the pure $BaBiO_3$ composition. In $Ba_{1-x}K_xBiO_3$, such a compound is created by substituting the Ba site and hence leaves the conducting Bi–O sublattice intact. The evidence for a CDW relies entirely on electron diffraction studies. The initial study of Pei *et al* [6] 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* [7] 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. Neither study provided a clear microscopic explanation for the observed modulation although Hewat *et al* [7] concluded that it did not result from the ordering of oxygen vacancies or potassium substitutional defects. Additional electron diffraction studies by Pei [1] confirmed the linear dependence of the incommensurate wavevector with the potassium content but such satellites could not be observed by neutron diffraction [1, 8]. The most detailed electron diffraction study by Verwerft *et al* [9] confirmed the presence of incommensurate satellites in both the semiconducting and superconducting phases.

Such observations have led to speculation as to the nature of the unirradiated state of this material. A variety of models involving a 'local CDW' which has a charge–mass modulation extending only over short distances [10, 11] would render the detection of such satellites more difficult.

In this letter we report the first observations of a commensurate CDW using x-ray scattering techniques. Our results are thus at variance with a recent synchrotron x-ray study which failed to observe any CDW satellites [12].

The single crystals were grown at Tsing Hua University, Taiwan using low-temperature, isothermal, isopotential electrochemical deposition. This technique produces high-quality, large-crystal clusters from which single-crystals were collected [13]. The samples were characterized by magnetic measurements. The superconducting composition (sample A, $x \sim 0.4$) displays a high T_c (30 K) but with a broad (~8 K) superconducting transition. A second crystal grown by a similar technique by Professor S N Barilo [14] with a lower potassium content (sample B, $x \sim 0.15$) was semiconducting and did not show a superconducting transition down to 5 K.

The x-ray experiments were performed at the University of Edinburgh. The crystals were examined and aligned using Laue diffraction before being mounted on a two-circle triple-axis diffractometer. The diffractometer is mounted on a high-brilliance rotating anode generator operated at 2.7 kW with a Cu anode. The Cu Kα x-ray beam was selected and collimated by two flat (0001) pyrolytic graphite crystals used as the monochromator and analyser. Such an arrangement gives a relatively poor resolution (~ 0.6° FWHM for the sample (300) Bragg peak) but very high intensities and avoids any multiple scattering from higher energy harmonics. The resolution is principally determined by the graphite crystals as the sample mosaic width was independently measured as 0.01 Å^{-1} (FWHM) using germanium (111) crystals. The sample crystal surface was polished with diamond paste and mounted such that the a^*b^* scattering plane was accessible using reflection geometry. The beam size was reduced by primary slits down to $\sim 1 \times 2$ mm^2 and the crystal translated until a relatively clean profile of the Bragg peaks was obtained. Such a procedure ensures we are observing scattering 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.

The lattice parameter was refined from these to a value of 4.28 ± 0.005 Å. This value has a relatively large uncertainty due to the low number of Bragg reflections accessible with Cu Kα radiation in reflection geometry. Nevertheless, the lattice parameter confirms that the composition is approximately $\sim$0.4 and that we are indeed in the cubic phase. All of the peaks are well defined and show little increased mosaic width or structure indicative of a complex microstructure. A two-dimensional contour plot of the x-ray scattering centred on the (300) Bragg peak weak superstructure scattering is observed at the ($hk0$) half-integer positions (see figure 1(a)). These peaks have an intensity of typically 10^{-4} of that of the Bragg peaks. Other weak peaks (such as that at (3.31, $\overline{0.4}$, 0)) were occasionally observed but these were always irreproducible, being absent with further polishing or in other crystals with the same composition. We 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 1(b) which confirm their existence. The width of the superstructure peaks is comparable to the main Bragg peaks and is resolution limited.

The superstructure satellites we observe, as shown in figure 1 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 are, however, small compared to our instrumental resolution (e.g. peaks were found at (3.485, 0.01, 0) and (2.505, 0.5, 0)). We are, at this stage, thus uncertain whether such small deviations are true or merely caused by crystal centring errors. Similar results were obtained from other samples grown by the same group and from crystals obtained from different groups. These results give us confidence that the observations are a natural feature of $Ba_{1-x}K_xBiO_3$ crystals and not a peculiar effect of some particular microstructure found in one crystal. Our observation of half-integer ($hk0$) reflections is evidence of an enlarged supercell. This is consistent with the existence of a CDW caused by ordered disproportionation of non-equivalent Bi^{3+} and Bi^{5+} ions. Low-temperature studies were also completed and gave very similar results to those obtained at room temperature. Superstructure satellites can be observed at half-integer positions indicating that the charge-density wave still exists even in the superconducting state. Further studies, using higher resolution are planned to measure any small variation of position and intensity with temperature.

Scans taken through positions where ⟨110⟩ incommensurate satellites had been reported by electron diffraction failed to find any evidence of x-ray scattering. Any such satellites would thus be at least an order of magnitude weaker than the commensurate superstructure reflections we are reporting. In this respect we are in agreement with the synchrotron study by Wochner *et al* [12] that such incommensurate satellites do not exist in unirradiated samples and we thus believe that the reported electron-diffraction results are indeed induced by electron-beam effects. However, in the electron-diffraction patterns of Verwerft *et al* [9] and of Zhou *et al* [15] it can be seen that in addition to the reported incommensurate reflections there are also satellites at (0.5, 0.5, 0), (1.5, 0.5, 0) (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. unlike in our work. The above authors fail to discuss the origin (or even the existence) of such commensurate satellites. Given our inability to observe the incommensurate satellites at

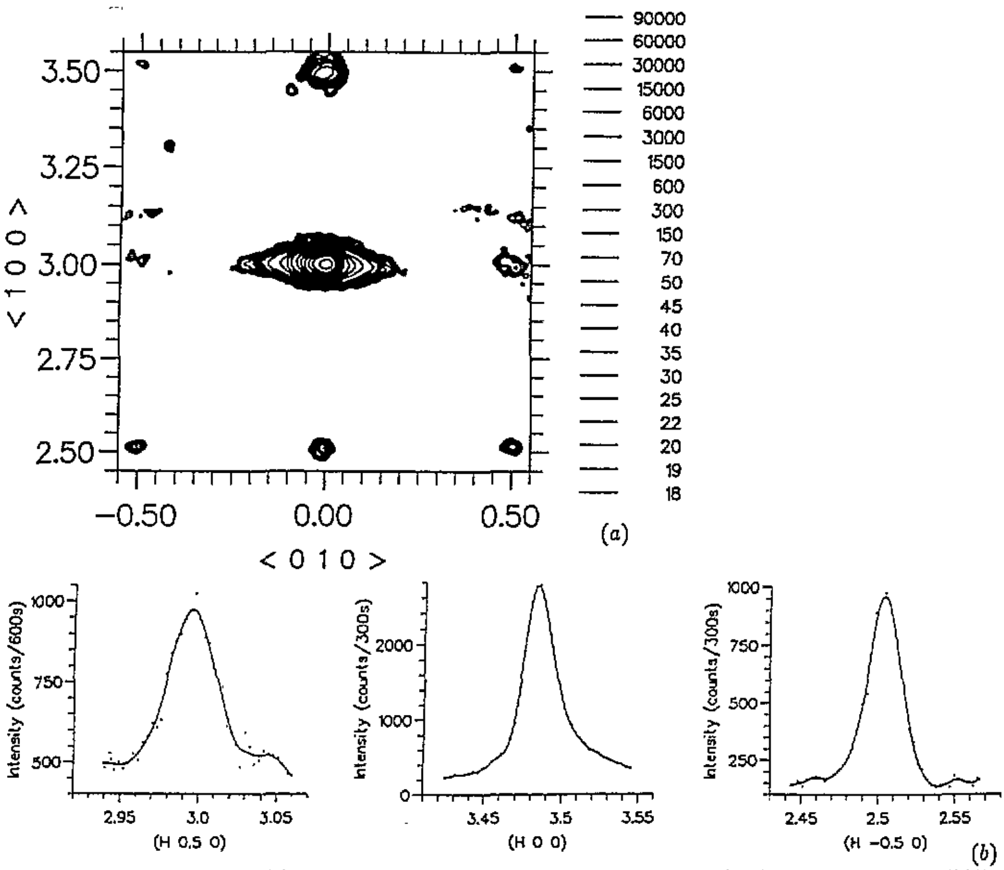

Figure 1. (*a*) An isointensity contour plot of the x-ray scattering intensity around the (300) Bragg peak from a superconducting composition (sample A, $x = 0.4$) at room temperature using pyrolytic graphite monochromator and analyser crystals. The contour levels displayed to the right were chosen to accentuate the weaker features; (*b*) One-dimensional scans along a^* through the superstructure satellites (3.5, 0.0) (3, 0.5, 0) and (2.5, $\overline{0.5}$, 0) at $T = 295$ K. The solid lines are guides to the eyes.

$q = (6 - \varepsilon)\ [110]_p^*$ [6] we believe that the different studies are observing fundamentally different phenomena.

In general, CDWs suppress superconductivity and vice versa [16]. 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. The latter transition is responsible for the presence of a superconducting state at low temperatures ($T_c = 2.8$ K) and high pressures ($P = 5.5$ kbar). Theoretical studies have shown that metallic CDW states can be formed by a Peierls distortion within the framework of the BCS model [17] when the CDW is imperfectly nested.

Measurements on a semiconducting crystal were also performed at room temperature. Overall there is considerable similarity to the results obtained from the metallic or superconducting compositions. Superlattice reflections were observed to surround the (300) Bragg peak at half integer positions along the [100], [010] and [110] directions, scans through the (3.5, 0, 0), (2.5, 0.5, 0) and (3, 0.5, 0) peaks confirming their existence. The positions of the superlattice reflections are either on or very close to the half-integer positions. The major difference between the two compositions was found by a scan in the [100] direction (see figure 2). 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 can now be seen. Such peaks are evidence of a larger supercell or incommensurate structure. Chaillout *et al* [18] studied oxygen deficient $BaBiO_{3-y}$ using x-ray and electron diffraction and observed incommensurate satellites with wavevectors $G_1 = +0.34a^*$ and $G_2 = +0.34b^*$ in the $(hk0)$ reciprocal plane around the Bragg spots. Our results are thus in close accord with those of Chaillout *et al*. We were unsuccessful in our search for other satellites such as (1.33, 0, 0) or (2.33, 0, 0) but this may simply be due to their lower intensity. Other satellites such as (3.0, 0.33, 0) could not be reliably found due to the large mosaic streak from the neighbouring Bragg reflection. The effect of this additional modulation on the transport properties is at this stage unclear. However, it is known that in the single-particle energy spectrum the incommensurability creates a set of discrete energy levels which may enhance the band gap at the Fermi surface [19].

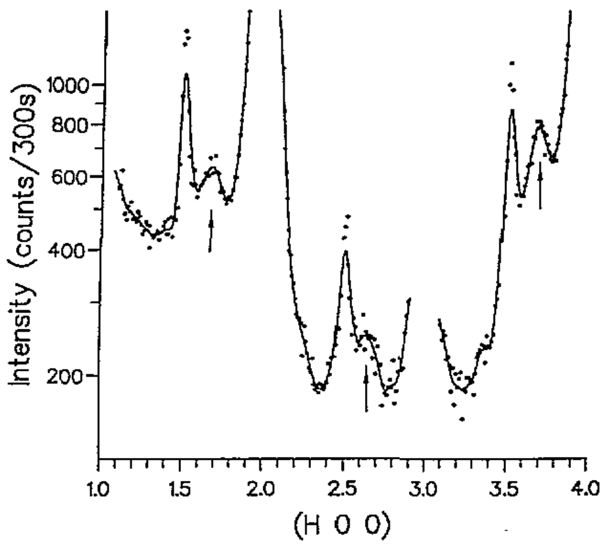

Figure 2. A one-dimensional scan along a^* from (100) to (400) displaying the subcell Bragg peaks ((200), (300)) superstructure satellites ((1.5, 0, 0), (2.5, 0, 0) and (3.5, 0, 0)) and additional weak features at (1.67, 0, 0), (2.67, 0, 0) and (3.67, 0, 0).

Finally, we address the question of why such a CDW-induced supercell has not been previously observed in other studies. Neutron diffraction studies [20] or powder x-ray diffraction measurements [8] do not have sufficient sensitivity to detect the weak superlattice reflections reported in this paper. The major discrepancy is with the single-crystal study using synchrotron x-ray radiation of Wochner *et al* [12]. Their study reported that no CDW satellites were observable in all ⟨110⟩ equivalent directions of an intensity greater than approximately 10^{-5} that of the (400) Bragg reflection. The major difference between their experimental set-up and ours is the instrumental resolution. The natural collimation of synchrotron radiation is well matched to the rocking curve widths of highly perfect silicon and thus their instrumental resolution is approximately one hundred times greater than in our experiments which employed pyrolytic graphite. It is this relaxed resolution which has enabled us to observe such weakly scattering phenomena with a conventional x-ray source. The high resolution obtainable with silicon optics can be disadvantageous in the search for reflections as centring errors are that much more important, as also is the density of observations required to ensure the observation of a sharp satellite. It is thus possible, that in spite of the considerable precautions undertaken by Wochner *et al* they missed such reflections. Another possible explanation is that the CDW-induced superlattice reflections are slightly incommensurate and thus slightly offset from the half-integer positions. This would be difficult to detect in our experiments but would shift the reflections away in ⟨110⟩ directions from integer Bragg positions and thus render them unobservable in high-resolution scans. Such a high instrumental resolution would also be disadvantageous if the CDW induced satellites were considerably broader than the integer Bragg reflections. This could arise if the CDW was localized rather than long range, hence broadening the superlattice reflections. A local CDW model has been theoretically proposed in the lead-doped series $BaPb_{1-x}Bi_xO_3$ [10, 11] and has received some experimental support from optical [5] and EXAFS measurements [21]. Further experiments at intermediate resolution are currently being undertaken on both the lead- and potassium-doped series to critically examine this suggestion and will be reported in the near future.

In summary, we have observed superlattice reflections at half-integer positions in single crystals of $Ba_{1-x}K_xBiO_3$. Such reflections are evidence of a larger supercell due to the presence of a charge-density wave caused by ordered disproportionation of Bi(IV) into non-equivalent Bi(III) and Bi(V) ions. This commensurate modulation has been found to persist from low temperatures to room temperature and exists in both semiconducting ($x < 0.37$) and superconducting ($x > 0.37$) compositions. A further incommensurate modulation has been observed in the semiconducting composition indicating the importance of such effects on the properties of this material. Previously proposed CDW satellites seen along ⟨110⟩ directions by electron diffraction are seemingly caused by electron-beam-induced irradiation and are not observed in unirradiated samples by x-ray diffraction.

We are grateful to H Vass for his excellent technical assistance throughout and to C M Lei for the magnetization measurements for characterizing the samples. We are grateful to Professor S N Barilo for the semiconducting crystal that we studied. Partial financial support for our programme was obtained from the Science and Engineering Research Council.

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