RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 39, NUMBER 1 1 JANUARY 1989

Charge-density waves and superconductivity in the $Ba_{1-x}K_xBiO_{3-y}$ system

Shiyou Pei, N. J. Zaluzec, J. D. Jorgensen, B. Dabrowski, D. G. Hinks,
A. W. Mitchell, and D. R. Richards
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439
(Received 15 August 1988; revised manuscript received 11 October 1988)

Electron diffraction confirms the existence of a cubic phase and a phase having a $\sqrt{2}a\times\sqrt{2}a\times 2a$ supercell in the $Ba_{1-x}K_xBiO_3$ system. It is also found that the supercell phase displays an additional incommensurate structural modulation along the [110] cubic direction. Since the modulation is observed in the semiconducting supercell phase and not in the superconducting cubic phase, such an observation leads to speculation that superconductivity in the $Ba_{1-x}K_xBiO_3$ system is associated with the disappearance of a charge-density wave.

The relationship between charge-density waves and superconductivity has been studied in a number of superconducting systems. In general, the charge-density wave (CDW) and superconductivity compete with one another, with the CDW tending to suppress superconductivity and vice versa.[1] In the case of a large enough CDW, i.e., where a gap is formed over the entire Fermi surface, the CDW produces a semiconducting state and destroys superconductivity. Such is the case, for example, in the Chevrel-phase superconductors with divalent cations where the compounds with triclinic structures (e.g., $BaMo_6S_8$ and $EuMo_6S_8$) are not superconducting because a gap has been opened at the Fermi surface, splitting a half-filled conduction band.[2] A small number of systems, however, exhibit the coexistence of CDW's and superconductivity. In the case of $2H$-$NbSe_2$, Raman scattering measurements have shown that the CDW gap is present in the superconducting state.[3-5] This result highlighted the importance of coupling between the superconducting electrons and the CDW phonon, and has given rise to various theories attempting to explain the nature of that coupling.[6-8] It has been unclear whether the coupling between the CDW and superconductivity actually raises T_c or simply reduces the amount of suppression that would otherwise occur.

More recent work has focused on the interaction between CDW's and superconductivity in the $BaPb_{1-x}Bi_xO_3$ system. This system exhibits superconductivity with T_c varying from 0.45 K for $x=0$ to 13 K for $x\approx 0.25$ and becomes semiconducting for $x>0.3$.[9,10] The semiconducting behavior is the result of a commensurate CDW involving the ordering of Bi^{3+} and Bi^{5+} into distinct crystallographic sites.[11-14] Just as in the Chevrel phases,[2] the highest T_c is observed at a composition adjacent to an instability in which the CDW opens a gap in the Fermi surface. The importance of the relationship between the CDW and superconductivity in the $BaPb_{1-x}Bi_xO_3$ system was further emphasized by recent optical reflectivity measurements by Tajima *et al.*, in which they show that the CDW energy gap exists as what they call a "pseudogap" in the metallic region ($0.15<x<0.3$).[15] They observe this pseudogap to change smoothly with x into a "true" gap for $x>0.3$. This important discovery has led Machida to propose that T_c is enhanced by the CDW in the $BaPb_{1-x}Bi_xO_3$ system.[16] In his theory, the enhancement of T_c results from a gap-edge singularity associated with the CDW which increases the density of states at the Fermi energy.

The recent discovery of superconductivity in the $Ba_{1-x}K_xBiO_3$ system was motivated by the idea that an appropriate doping method might suppress the commensurate CDW associated with semiconducting $BaBiO_3$ and create a metallic (and superconducting) compound closer to the half-filled-band condition (i.e., closer to the undoped $BaBiO_3$ composition) than had been achieved in the case of $BaPb_{1-x}Bi_xO_3$.[17-19] It was speculated that such a compound might exhibit a higher T_c because of a stronger electron-phonon interaction near the pure $BaBiO_3$ composition. Thus, in the $Ba_{1-x}K_xBiO_3$ system, a metallic, superconducting compound is created by leaving the conducting Bi-O sublattice intact and, instead, doping substitutionally at the Ba site. A T_c of 30 K is achieved in $Ba_{1-x}K_xBiO_3$, in contrast to the maximum T_c of 13 K in $BaPb_{1-x}Bi_xO_3$.[18,20]

Our initial study of the electronic and structural properties of the $Ba_{1-x}K_xBiO_{3-y}$ system versus x was consistent with the expected interplay between CDW's and superconductivity.[20] We observed superconductivity only in a cubic phase which exists for $x>0.25$. For $x<0.25$, the structure is body-centered tetragonal with a $\sqrt{2}a\times\sqrt{2}a\times 2a$ supercell (where a is the cubic lattice constant), similar to the monoclinic $BaBiO_3$ cell of the same dimensions,[12,13] and semiconducting behavior is observed. The highest T_c is obtained for compositions adjacent to the phase transition.

Even though our neutron-diffraction data for the semiconducting $\sqrt{2}a\times\sqrt{2}a\times 2a$ supercell phase could be perfectly indexed on a body-centered-tetragonal cell (with a near-zero tetragonal strain), we were unable to determine a unique solution for the structure. In particular, we were unable to confirm whether this structure involves a commensurate CDW arising from Bi^{3+}-Bi^{5+} ordering as in undoped $BaBiO_3$. Thus, in order to more fully investigate the structural behavior in the $Ba_{1-x}K_xBiO_3$ system, the electron diffraction studies reported here were performed. Electron diffraction is particularly sensitive to supercell reflections (including reflections which may be too weak to observe in the neutron-diffraction data) arising partial-

ly from the fact that the strong reflections from the basic cell are attenuated by primary extinction. Thus, electron diffraction provides a sensitive test of the existence of the cubic phase as well as a probe of any subtle structural modulation. In our electron-diffraction studies, we observe the same cubic and $z=4$ body-centered-tetragonal structures previously reported.[20] Unexpectedly, we also observe an additional incommensurate modulation of the tetragonal structure in the [110] cubic direction with a wavelength which varies between $4d_{(110)}$ and $5d_{(110)}$ [where $d_{(110)}$ is the separation between two (110) cubic planes].

Samples having the initial composition $Ba_{0.6}K_{0.4}BiO_3$, $Ba_{0.67}K_{0.33}BiO_3$, and $Ba_{0.8}K_{0.2}BiO_3$ were made using the two-step synthesis method described previously.[20,21] According to the neutron-diffraction studies, which provide a measure of the K concentration in the $Ba_{1-x}K_xBiO_3$ phase, the final compositions of these samples should fall within the superconducting cubic phase ($x \approx 0.3$), a mixture of both phases, and the semiconducting supercell phase ($x \approx 0.2$), respectively. Specimens for transmission electron microcopy (TEM) and selected-area-diffraction (SAD) studies were made by direct grinding and also by ion milling of the mechanically thinned slabs. In the case of the latter technique, it was necessary to employ low ion beam energies during the final stage of the milling process in order to minimize the formation of a thin polycrystalline surface layer. The specimens were examined at room temperature using a Phillips 420 or JEOL electron microscope operated at 100 keV.

Major reflections of SAD patterns taken for all specimens can be indexed in terms of a cubic perovskite structure. For the $Ba_{0.6}K_{0.4}BiO_3$ sample a cubic phase is observed. Since the body-centered-tetragonal phase with axes $\sqrt{2}a \times \sqrt{2}a \times 2a$ will give an electron-diffraction pattern identical to the cubic phase along some cubic zone axes such as [100], [010], and ⟨111⟩, the observation of independent patterns cannot lead to a definite conclusion of whether a truly cubic structure exists. Instead, a set of related SAD patterns obtained from the same area is needed. Figure 1 depicts such a set of patterns. Since in a $\sqrt{2}a \times \sqrt{2}a \times 2a$-type structure at least one of the two ⟨110⟩ patterns which are oriented 60° apart must show superlattice reflections that characterize the larger $\sqrt{2}a \times \sqrt{2}a \times 2a$-type supercell (as illustrated by the [101] section shown in Fig. 4), these patterns confirm the existence of the cubic phase.

For the samples of starting compositions $Ba_{0.67}K_{0.33}BiO_3$ and $Ba_{0.8}K_{0.2}BiO_3$ (and for a small number of grains in the $Ba_{0.6}K_{0.4}BiO_3$ sample), additional superlattice reflections are observed in the electron-diffraction patterns. As expected, some of these superlattice reflections agree with the body-centered-tetragonal $\sqrt{2}a \times \sqrt{2}a \times 2a$ supercell previously observed by neutron diffraction.[20] Some of the patterns, however, reveal additional spots which are not located at positions of simple fractions between two major cubic reflections. This modulation is, therefore, incommensurate with the cubic lattice. An example of such a diffraction pattern for a selected area of the $Ba_{0.6}K_{0.4}BiO_3$ sample is shown in Fig. 2. The observed modulation is along the ⟨110⟩ cubic directions. For this

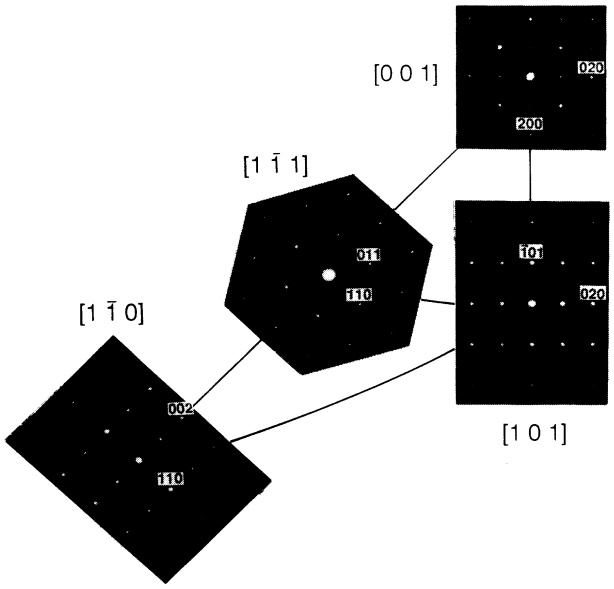

FIG. 1. Electron diffraction patterns from the same selected area of the sample having starting composition $Ba_{0.6}K_{0.4}BiO_3$, demonstrating the existence of a cubic phase.

grain, the wavelength of the modulation is $4.34d_{(110)}$. In general, the modulation wavelength varies between $4d_{(110)}$ and $5d_{(110)}$. Using the lattice imaging technique, it was found that this modulated phase consists of small domains about 15 nm in dimensions (see Fig. 3). Within each domain, the modulation appears to occur along only one of the ⟨110⟩ directions. Because of the small domain size, SAD patterns often consist of a superposition of diffraction coming from multiple domains having perpendicular orientations, as shown in Fig. 2.

In all of the data we have taken, the incommensurately

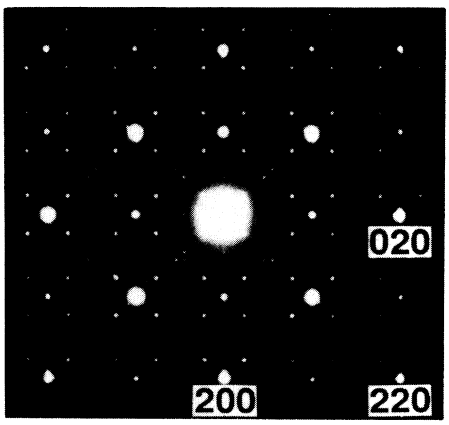

FIG. 2. Selected-area electron diffraction pattern taken from the sample having starting composition $Ba_{0.6}K_{0.4}BiO_3$, showing an incommensurate structural modulation with a wavelength of $4.34d_{(110)}$. The pattern is indexed in terms of the pseudocubic cell.

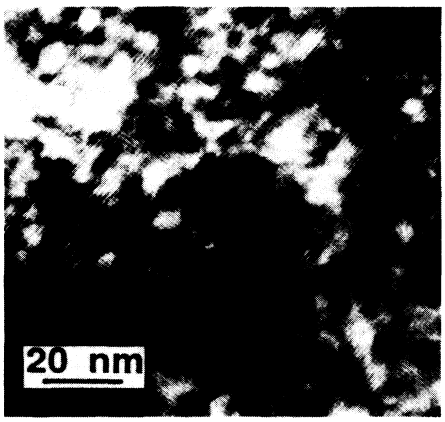

FIG. 3. Lattice image showing that the modulation in a supercell phase grain in the $Ba_{0.6}K_{0.4}BiO_3$ sample takes place only along one of the cubic ⟨110⟩ directions.

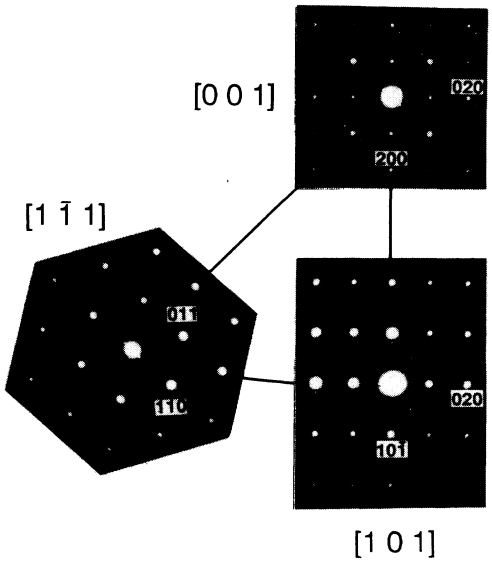

FIG. 4. Selected-area electron diffraction patterns showing that the incommensurate modulation observed in the $Ba_{0.8}K_{0.2}BiO_3$ sample is accompanied by a commensurate $\sqrt{2}a\times\sqrt{2}a\times 2a$ supercell. The modulation wavelength is $4.89d_{(110)}$. The pattern is indexed in terms of the pseudocubic cell.

modulated structure is associated with the $\sqrt{2}a\times\sqrt{2}a\times 2a$ supercell. This can be seen in Fig. 4, which shows a set of SAD patterns obtained by tilting the same selected area to three different orientations. The observation of superlattice reflections in the [101] section is direct evidence of the $\sqrt{2}a\times\sqrt{2}a\times 2a$ supercell.

By comparing SAD patterns for the three samples, we conclude that the abundance of the modulated phase and the wavelength of the modulation both vary inversely with K concentration. Unfortunately, it is difficult to quantify this observation because the K concentration may not be homogeneous in a given sample,[20] and because the grains observed by electron diffraction may not be a statistical representation of the bulk. However, some important general conclusions can be drawn. With decreasing K concentration, we observe an increase of areas showing such a modulation. For example, in the sample having the starting composition $Ba_{0.8}K_{0.2}BiO_3$, every area under examination shows some degree of modulation, while modulation is seen in only a small fraction of the grains in samples having the starting composition $Ba_{0.6}K_{0.4}BiO_3$. In addition, the modulation wavelength was found to be $4.00d_{(110)}$–$4.43d_{(110)}$ in the sample having the starting composition $Ba_{0.6}K_{0.4}BiO_3$, $4.17d_{(110)}$–$4.52d_{(110)}$ in the $Ba_{0.67}K_{0.33}BiO_3$ sample, and $4.66d_{(110)}$–$4.93d_{(110)}$ in the $Ba_{0.8}K_{0.2}BiO_3$ sample. Thus, the modulation wavelength appears to vary inversely with K concentration and has the smallest value, $4d_{(110)}$, at the composition which separates the cubic and tetragonal phases. According to our previous neutron studies, this composition is $x\approx 0.25$.[20]

From these results alone, it is not possible to determine the cause of the incommensurate modulation. The observation that the modulation wavelength varies with the K concentration suggests that ordering of K in the structure may be involved. A model which assumes ordering of K and Ba atoms (space group *Pmm*2) agrees reasonably well with the observed SAD patterns. Additionally, such a model predicts a small intensity [0.02% of the cubic (110) peak] for the incommensurate superlattice reflections for neutron diffraction, explaining our failure to observe the incommensurate modulation by neutron diffraction.

In support of this hypothesis, we find that when grains of the cubic phases are subjected to an intense exposure of a converged electron beam, additional spots corresponding to the structural modulation gradually occur. At the same time, the K characteristic x-ray peaks in an energy dispersive spectrum tend to decrease, indicating a loss of K in the beam-heated area. However, during electron beam heating, we would also expect oxygen loss. Consequently, we cannot exclude the occurrence of an ordering of oxygen vacancies. Indeed, the observation of weak satellites by single-crystal x-ray diffraction and electron diffraction in $BaBiO_{3-y}$ has been interpreted by Chaillout and Remeika based on oxygen vacancy ordering.[22]

It should be stressed that such models based on substitutional or vacancy ordering are not unique explanations for the observed modulation. Indeed, calculations of the electronic structure of $Ba_{0.5}K_{0.5}BiO_3$ for various ordered supercells show a minimal effect on the electron states near the Fermi energy and suggest that K ordering may be unlikely.[19] Moreover, atomic displacement, involving either the oxygen or metal ions, is an equally valid explanation for the modulation.

In summary, by using electron diffraction, we have confirmed the existence of a cubic phase and a phase having a $\sqrt{2}a\times\sqrt{2}a\times 2a$ supercell in the $Ba_{1-x}K_xBiO_3$ system. The cubic phase is free from any structural modulation, while (for the K compositions studied here) the supercell phase involves an additional incommensurate structural modulation along the [110] cubic direction.

Thus, the semiconducting behavior for $x < 0.25$ could result not only from a commensurate CDW arising from Bi^{3+}-Bi^{5+} ordering as in the case of the $BaPb_{1-x}Bi_xO_3$ system, but also from an additional incommensurate CDW modulation whose origin is not yet understood. Since structural modulations are observed only in the semiconducting $\sqrt{2}a \times \sqrt{2}a \times 2a$ supercell phase and not in the cubic phase, we speculate that superconductivity in the $Ba_{1-x}K_xBiO_3$ system is associated with the disappearance of a CDW in a way that is analogous to the role played by antiferromagnetism, or spin-density waves (SDW), in Cu-based oxide superconducting systems.[23]

The authors wish to thank R. E. Cook and A. Philippides of the Argonne Electron Microscopy Center for much technical assistance. This work is supported by the U.S. Department of Energy, Basic Energy Sciences —Material Sciences, under Contract No. W-31-109-ENG-38.

[1]C. A. Balseiro and L. M. Falicov, in *Superconductivity in d- and f-Band Metals,* edited by H. Suhl and M. B. Maple (Academic, New York, 1980), pp. 105–112.

[2]See, for example, J. D. Jorgensen, D. G. Hinks, and G. P. Felcher, Phys. Rev. B **35**, 5365 (1987), and references cited therein.

[3]R. Sooryakumar and M. V. Klein, Phys. Rev. Lett. **45**, 662 (1980).

[4]R. Sooryakumar and M. V. Klein, Phys. Rev. B **23**, 3213 (1981).

[5]R. Sooryakumar, M. V. Klein, and R. F. Frindt, Phys. Rev. B **23**, 3222 (1981).

[6]C. A. Balseiro and L. M. Falicov, Phys. Rev. Lett. **45** 662 (1980).

[7]D. A. Brown and K. Levin, Phys. Rev. B **28**, 4029 (1983).

[8]A. L. Kasatkin and E. A. Pashitski, Fiz. Nizk. Temp. **10**, 63 (1984) [Sov. J. Low Temp. Phys. **10**, 32 (1984)].

[9]V. V. Bogatko and Yu. N. Venevtsev, Fiz. Tverd. Tela (Leningrad) **22**, 1211 (1980) [Sov. Phys. Solid State **22**, 705 (1980)].

[10]See S. Uchida, K. Kitazawa, and S. Tanaka, Phase Trans. **8**, 95 (1987), and references cited therein.

[11]D. E. Cox and A. W. Sleight, in *Proceedings of the Conference on Neutron Scattering, Gatlinburg, Tennessee, 1976,* edited by R. M. Moon (National Technical Information Service, Springfield, VA, 1976), pp. 45–54.

[12]D. E. Cox and A. W. Sleight, Solid State Commun. **19**, 969 (1976).

[13]D. E. Cox and A. W. Sleight, Acta Crystallogr. Sect. B **35**, 1 (1979).

[14]L. F. Matteiss and D. R. Hamann, Phys. Rev. B **28**, 4227 (1983).

[15]S. Tajima, S. Uchida, A. Masaki, H. Takagi, K. Kitazawa, S. Tanaka, and S. Sugai, Phys. Rev. B **35**, 696 (1987); S. Tajima *et al., ibid.* **32**, 6302 (1985); S. Uchida *et al.*, J. Phys. Soc. Jpn. **54**, 4395 (1985).

[16]K. Machida, Physica C **156**, 276 (1988).

[17]L. F. Mattheiss, E. M. Gyorgy, and D. W. Johnson, Jr., Phys. Rev. B **37**, 3745 (1988).

[18]R. J. Cava, B. Batlogg, J. J. Krajewski, R. C. Farrow, L. W. Rupp, Jr., A. E. White, K. T. Short, W. F. Peck, Jr., and T. Y. Kometani, Nature **332**, 814 (1988).

[19]L. F. Mattheiss and D. R. Hamann, Phys. Rev. Lett. **60**, 2681 (1988).

[20]D. G. Hinks, B. Dabrowski, J. D. Jorgensen, A. W. Mitchell, D. R. Richards, Shiyou Pei, and Donglu Shi, Nature **333**, 836 (1988).

[21]D. G. Hinks, D. R. Richards, B. Dabrowski, A. W. Mitchell, J. D. Jorgensen, and D. T. Marx, Physica C **156**, 477 (1988).

[22]C. Chaillout and J. P. Remeika, Solid State Commun. **56**, 833 (1985).

[23]S. K. Sinha, Mater. Res. Soc. Bull. **13**, 24 (1988), and references cited therein.

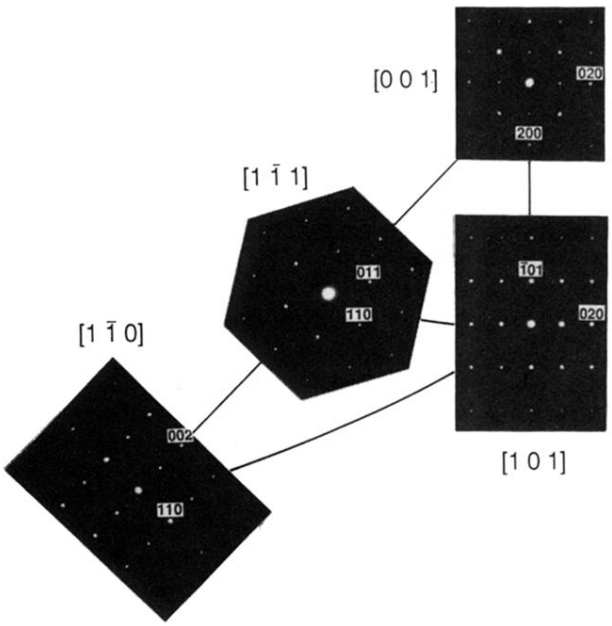

FIG. 1. Electron diffraction patterns from the same selected area of the sample having starting composition $Ba_{0.6}K_{0.4}BiO_3$, demonstrating the existence of a cubic phase.

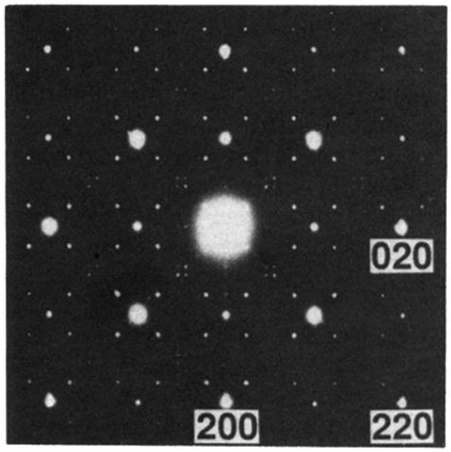

FIG. 2. Selected-area electron diffraction pattern taken from the sample having starting composition $Ba_{0.6}K_{0.4}BiO_3$, showing an incommensurate structural modulation with a wavelength of $4.34d_{(110)}$. The pattern is indexed in terms of the pseudocubic cell.

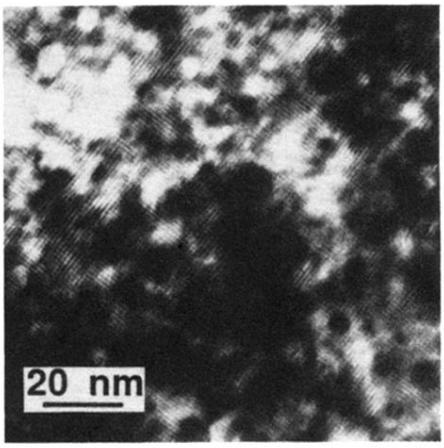

FIG. 3. Lattice image showing that the modulation in a supercell phase grain in the $Ba_{0.6}K_{0.4}BiO_3$ sample takes place only along one of the cubic $\langle 110 \rangle$ directions.

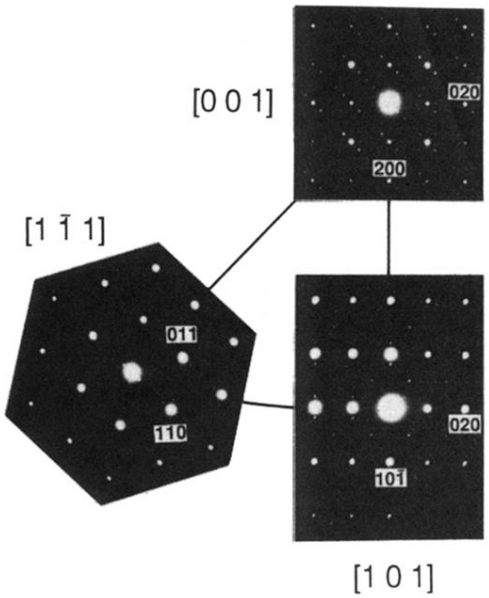

FIG. 4. Selected-area electron diffraction patterns showing that the incommensurate modulation observed in the $Ba_{0.8}K_{0.2}BiO_3$ sample is accompanied by a commensurate $\sqrt{2}a \times \sqrt{2}a \times 2a$ supercell. The modulation wavelength is $4.89d_{(110)}$. The pattern is indexed in terms of the pseudocubic cell.