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1989 J. Phys.: Condens. Matter 1 2939

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LETTER TO THE EDITOR

Superconductivity in $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ and $\text{Ba}_x\text{K}_{1-x}\text{BiO}_3$

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Received 7 February 1989, in final form 13 March 1989

Abstract. The superconducting transition temperatures of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ (BPB) and $\text{Ba}_x\text{K}_{1-x}\text{BiO}_3$ (BKB) are evaluated on the basis of the strong-coupling theory. The electron–lattice interaction is calculated microscopically by using the realistic electronic band structure. It is shown that the superconducting properties of BKB, such as high transition temperatures (≈ 30 K) and rather small isotope effects, can be understood within the phonon mechanism.

The oxide superconductor $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ (BPB) has attracted much attention because of its interesting superconducting properties. Superconductivity in BPB has been observed in the composition range $0 < x < 0.35$ and the maximum transition temperature T_c is about 13 K ($x = 0.25$) (Sleight *et al* 1975, Thanh *et al* 1980). Recently $\text{Ba}_x\text{K}_{1-x}\text{BiO}_3$ (BKB) has been found to have the highest T_c (≈ 30 K at $x = 0.7$) among the oxide superconductors not containing Cu ions (Mattheiss *et al* 1988, Cava *et al* 1988, Hinks *et al* 1988). Both BPB and BKB have a simple perovskite-type structure and do not contain any transition-metal element. Thus a magnetic mechanism may not be expected for the superconductivity in these compounds. Therefore, it is of interest to investigate the electron–lattice interaction microscopically, in order to clarify the mechanism of the superconductivity in BPB and BKB.

We have studied microscopically the electron–lattice interaction and the lattice dynamics of BPB in the range $0 < x < 0.35$ (Shirai *et al* 1986, 1989). Our calculation is based on fitting tight-binding parameters to band structures obtained by a first-principles method, and differentiating them to obtain matrix elements of the electron–lattice interaction (Peter *et al* 1974, 1977, Varma *et al* 1979, Motizuki and Suzuki 1986). The electronic bands of BPB obtained by the LAPW method (Mattheiss and Hamann 1983) have been used in our calculation. We have also calculated the spectral function $\alpha^2F(\omega)$ (Shirai *et al* 1989) in order to provide a basis on which to discuss quantitatively the superconducting properties of BPB in the framework of a strong-coupling theory of the phonon mechanism. The purpose of this Letter is, firstly, to extend our investigation to a wider composition range ($0 < x < 1$) which covers the superconducting composition of BKB and, secondly, to give an accurate evaluation of T_c by solving the Eliashberg equations (Bergmann and Rainer 1973) using the calculated spectral function $\alpha^2F(\omega)$. We also present a theoretical estimation of the isotope shift of T_c caused by replacing ^{16}O with ^{18}O .

The electronic band structure of BPB has been calculated by Mattheiss and Hamann using the LAPW method (Mattheiss and Hamann 1983). According to their results the conduction band which crosses the Fermi level is a hybridised band consisting of O 2p and Bi (or Pb) 6s and 6p orbitals. This conduction band is well reproduced by the tight-binding (TB) model with three Slater–Koster transfer integrals between nearest-neighbouring O and Bi (or Pb) atoms. By using this TB conduction band we have calculated the electron–lattice coupling coefficient $g_{\mu}^{\alpha}(\mathbf{k}, \mathbf{k}')$, which represents the strength of the coupling between two conduction band states \mathbf{k} and \mathbf{k}' caused by displacement of the μ th atom along the α direction ($\alpha = x, y, z$). In an actual calculation it is necessary to evaluate the derivatives of transfer integrals t' . By taking into consideration electronic band structures in a distorted phase of BaBiO₃ we have estimated the value of t' as $t' \approx 4\text{--}5 \text{ eV } \text{\AA}^{-1}$. Recently Mattheiss and Hamann (1988) calculated the band structure for the ordered alloy Ba_{0.5}K_{0.5}BiO₃, and it is confirmed that the conduction band of BaBiO₃ is little affected by substitution of K for Ba. Therefore we adopt the rigid-band approximation for the doping effects, i.e. we assume that as x increases the TB conduction band is filled gradually without change of its dispersion. At $x = 0$ the conduction band is empty and at $x = 1$ it is half-filled.

Next we investigate the lattice dynamics in this system including the effect of the electron–lattice interaction. The dynamical matrix is divided into two parts: the generalised electronic susceptibility χ which is the Fourier transform of the effective long-range forces caused by the electron–lattice interaction and the remaining part D_0 . Usually D_0 is expressed as the Fourier transform of inter-atomic short-range forces. For D_0 we consider seven kinds of short-range forces. They have been determined so as to fit seven phonon frequencies observed in BaPb_{0.75}Bi_{0.25}O₃ (Reichardt and Weber 1987), which seem to be insensitive to the effect of the electron–lattice interaction. The calculation of χ has been performed by taking into account the wavevector and mode dependences of $g_{\mu}^{\alpha}(\mathbf{k}, \mathbf{k}')$, and then the phonon dispersion curves have been obtained by diagonalising the dynamical matrix $\chi + D_0$. The electron–lattice interaction has been found to lower the frequencies and to broaden the linewidth of the longitudinal (L) O-stretching and/or breathing mode vibration, which was originally located around 60 meV. The phonon frequency renormalisation shows remarkable dependences on the wavevector and x . For instance, for $x = 0.3$ a substantial renormalisation is seen, especially around the X point in the first Brillouin zone, while for $x > 0.4$ the phonon branch becomes soft around the M and R points as well as the X point. The wavevector and mode dependences of the phonon renormalisation originate from the wavevector and mode dependences of $g_{\mu}^{\alpha}(\mathbf{k}, \mathbf{k}')$. It is further noted that the magnitude of the phonon frequency renormalisation depends on the value of t' . When $t' = 4 \text{ eV } \text{\AA}^{-1}$ the phonon frequency does not show complete softening and the lattice is stable up to $x = 1$. Experimentally the structure of BaBiO₃ at room temperature is described by a frozen state of the O-breathing phonon just at the R point (Cox and Sleight 1976). We have confirmed that if we use a value of t' slightly larger than $4 \text{ eV } \text{\AA}^{-1}$, the frequency of the O-breathing phonon at the R point vanishes for $x = 1$ and hence the lattice becomes unstable against formation of the distorted structure corresponding to that phonon.

Now we discuss the superconductivity of BPB and BKB in the framework of the strong-coupling theory of the phonon mechanism. For this purpose we have calculated the spectral function $\alpha^2F(\omega)$ making use of the renormalised phonons obtained above. In figure 1 we show the spectral function $\alpha^2F(\omega)$ and the phonon density of states $F(\omega)$ calculated for several values of x for $t' = 4 \text{ eV } \text{\AA}^{-1}$. It is found that $\alpha^2F(\omega)$ has a frequency dependence entirely different from that of $F(\omega)$. It should be noted that $\alpha^2F(\omega)$ has

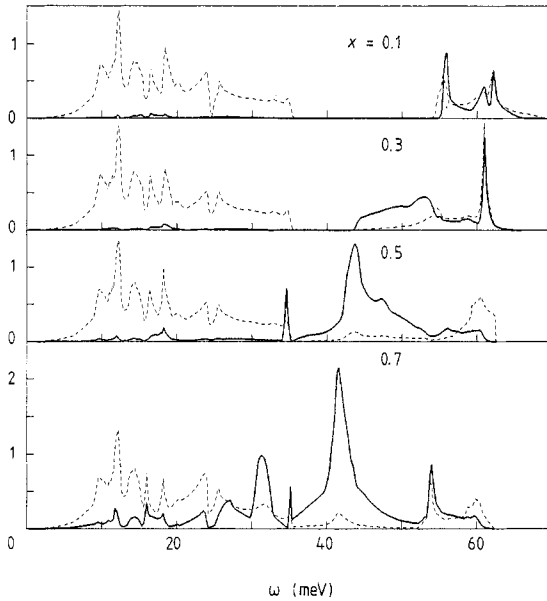


Figure 1. The spectral function $\alpha^2 F(\omega)$ (full curves) and the phonon density of states (broken curves) calculated for $x = 0.1, 0.3, 0.5$ and 0.7 for $t' = 4 \text{ eV \AA}^{-1}$. $\alpha^2 F(\omega)$ is a dimensionless quantity and the unit of $F(\omega)$ is $\text{meV}^{-1}/\text{unit cell}$.

some prominent structures in the frequency range of the O-stretching/breathing mode. Thus this O-stretching/breathing mode is expected to contribute dominantly to the superconductivity. As x increases, some main peaks in $\alpha^2 F(\omega)$ shift to the lower-frequency side, reflecting the phonon frequency renormalisation, and the magnitude of $\alpha^2 F(\omega)$ increases strikingly in the whole frequency range up to 60 meV. This considerable change in $\alpha^2 F(\omega)$ is expected to bring a remarkable dependence on x of T_c .

The transition temperature T_c has been evaluated by solving the linearised Eliashberg equations using the calculated $\alpha^2 F(\omega)$. The obtained dependences on x of T_c are shown in figure 2. For each x we have calculated T_c with four different values of μ^* , 0.0, 0.05, 0.1 and 0.15. Here μ^* denotes the effective screened Coulomb repulsion constant. In most superconductors μ^* has been taken empirically to be between 0.1 and 0.15. The calculated T_c increases rapidly with increasing x , and reaches 28 K for $x = 0.7$ in the case when $\mu^* = 0.1$. If we use a larger value of t' , we obtain a higher transition temperature as long as the lattice instability does not occur.

The dimensionless coupling constant λ has been evaluated to be 0.98 for $\mu^* = 0.1$ and $x = 0.7$ ($T_c = 28 \text{ K}$). It should be noted here that we must be careful in using McMillan's equation for T_c (McMillan 1968)

$$T_c = (\theta_D/1.45) \exp\{-1.04(1 + \lambda)/[\lambda - \mu^*(1 + 0.62\lambda)]\}$$

where θ_D denotes the Debye temperature. For BPB θ_D is estimated to be $\approx 190 \text{ K}$ (Itoh *et al* 1984). Then, if we use the above McMillan equation to estimate T_c for $\lambda = 0.98$ (μ^* is fixed at 0.1), we have $T_c = 10.5 \text{ K}$. On the other hand, if we determine the value of λ from this McMillan equation so as to get $T_c = 28 \text{ K}$, we obtain a very large value of λ , such as 3.0. Therefore it is not justified to utilise the McMillan equation with θ_D for evaluating T_c in such a complex system as BKB. Our results for T_c agree well with observed T_c for BKB, but disagree with those for BPB. One of the reasons for this discrepancy may be that the rigid-band model is inappropriate for describing BPB because in BPB the Pb

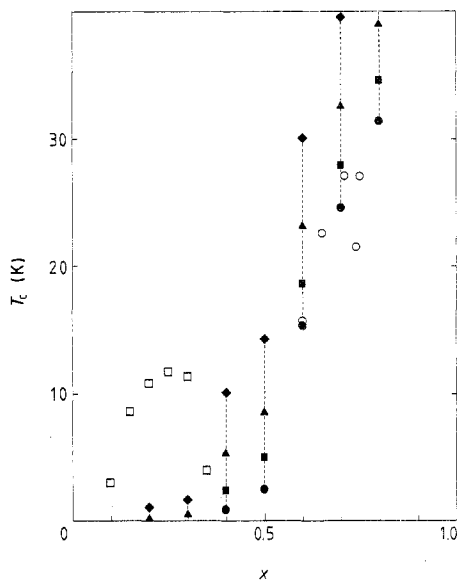


Figure 2. The superconducting transition T_c as a function of x . The calculation of T_c was for $\mu^* = 0.0$ (\blacklozenge), 0.05 (\blacktriangle), 0.10 (\blacksquare) and 0.15 (\bullet), respectively. The experimental data for BPPB (\square) (Thanh *et al* 1980) and for BKB (\circ) (Hinks *et al* 1988) are also shown.

Table 1. The isotope effect on T_c due to replacing ^{16}O with ^{18}O when $t' = 4 \text{ eV } \text{\AA}^{-1}$ and $x = 0.7$ ($\text{Ba}_{0.7}\text{K}_{0.3}\text{BiO}_3$).

M_0	16	18	α
λ	0.978	0.992	
T_c ($\mu^* = 0.0$)	39.61	37.99	0.33
($\mu^* = 0.05$)	32.56	31.35	0.30
($\mu^* = 0.10$)	27.93	27.00	0.27
($\mu^* = 0.15$)	24.61	23.87	0.24

atom, which is one of constitutive elements of the conduction band, is substituted randomly by the Bi atom.

Finally we have evaluated the isotope shift of T_c by calculating T_c when ^{16}O is replaced with ^{18}O . The results for $t' = 4 \text{ eV } \text{\AA}^{-1}$ and $x = 0.7$ are listed in table 1. A characteristic exponent α , defined by $T_c \propto M_0^{-\alpha}$ ($M_0 = \text{oxygen atomic mass}$), is found to be much smaller than the so-called BCS value ($\alpha = 0.5$): $\alpha = 0.33$ for $\mu^* = 0.0$ and $\alpha = 0.24$ for $\mu^* = 0.15$. Similar results for α are also obtained for a larger value of t' . Experimentally, the value of α is evaluated to be 0.21 by Batlogg *et al* (1988) and 0.35 by Kondoh *et al* (1989). The principal reason for α differing from the BCS value is that the vibration of atoms other than oxygens, such as Bi atoms, contribute appreciably to the superconductivity, particularly in the case where a substantial phonon frequency renormalisation is caused by the electron–lattice interaction. Recently Barbee *et al* (1988) have carried out calculations of α in compound superconductors by using a simplified model spectral function. They have also pointed out the possibility that the value of α may be much smaller than the BCS value for specific isotopic substitutions in compound superconductors.

In summary, we have investigated the lattice dynamics and the superconductivity of BPB and BKB in the framework of the strong-coupling theory of the phonon mechanism. Our results suggest that the superconducting properties of BKB, such as the magnitude of T_c and the isotope effect on T_c , can be understood within the phonon mechanism. It is particularly emphasised that the significant renormalisation of the L O-stretching/breathing mode phonons plays an important role in producing the high T_c in BKB. On the other hand, it is not yet known whether the superconductivity in BPB can be explained within the phonon mechanism. It seems that effects of random substitution of Bi for Pb have to be suitably taken into account.

This work is supported by a Grant-in-Aid of Scientific Research on Priority Areas (No 63631007) from the Ministry of Education, Science and Culture.

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