

# High- $T_c$ superconductivity in bismuthates— How many roads lead to high $T_c$ ?

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**The superconducting transition temperature in BaBiO<sub>3</sub>-based superconductors exceeds 30 K. Magnetic measurements are analyzed to give their density of states at  $E_F$ ,  $N^*(0) \propto \gamma$ . The uniqueness of Bi-O and Cu-O superconductors is revealed in an updated  $T_c$ - $\gamma$  plot. The two classes of compounds share basic electronic properties, particularly a partially unoccupied band with significant O 2p character, which might favor a common pairing mechanism.**

## Introduction

Superconducting transition temperatures around  $\sim 30$  K [1-3] in BaBiO<sub>3</sub>-based compounds are remarkable, as they exceed the  $T_c$ 's of all conventional superconductors. The cuprate-based superconductors [4], however, have  $T_c$ 's well in excess of 100 K, and the obvious question arises whether the same microscopic mechanism leads to pairing. Thus we may ask, "How many roads lead to high  $T_c$ ?" No firm

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answer can be given yet. Here we review measurements on Ba(Pb,Bi)O<sub>3</sub> and (Ba,K)BiO<sub>3</sub> from which we deduce the density of states,  $N^*(0)$ , and conclude that the Bi-O superconductors are "high- $T_c$  superconductors" when  $T_c$  is compared to  $N^*(0)$ . The basic electronic structure of the bismuthates and cuprates is very similar and distinctly different from other oxides. This might suggest a common mechanism for superconducting pairing.

## Bismuthate superconductors

In a somewhat simplified view of conventional pairing, a high transition temperature is favored by a high energy of the mediating excitations (phonons, etc.), by a high density of electronic states at the Fermi level, and finally by a strong coupling between those excitations and the electrons. In the following we present measurements on (Ba,K)BiO<sub>3</sub> and Ba(Pb,Bi)O<sub>3</sub> which provide information on some of the above aspects. In particular, the density of states  $N^*(0)$  at  $E_F$  is estimated and compared to band structure calculations, which in turn gives estimates for the dimensionless coupling parameter  $\lambda$ .

## Density of states at $E_F$

The most convenient and reliable procedure for estimating  $N^*(0)$  in superconductors with high  $T_c$ 's and small  $N^*(0)$  relies on a thermodynamic relationship which connects the slope of the thermodynamic critical field  $H'_c$  with the specific

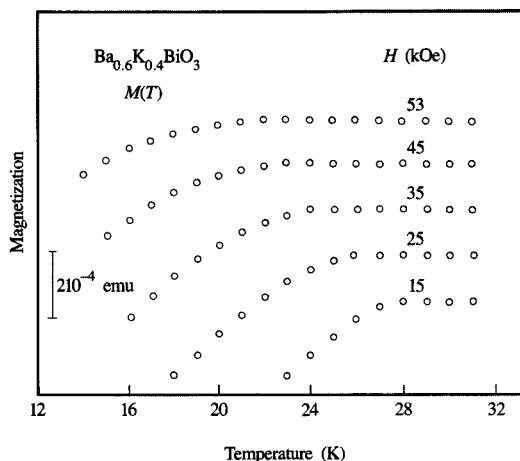
heat anomaly  $\Delta C$  at  $T_c$ , which in turn is proportional to  $N^*(0)$ . This is merely a consequence of the thermodynamics of a second-order phase transition, and thus is independent of microscopic details. For the compounds under discussion, using Rutgers' formula is particularly appealing because  $\Delta C$  at  $T_c$ , which is an extensive quantity, is deduced from two intensive quantities, the lower and upper critical fields. Thus, one does not rely on a fully superconducting volume as long as the unit cell volume of the superconductor is known. Furthermore, when the electronic contribution to the specific heat is small compared to the phononic part, specific heat measurements need to resolve anomalies on the 1% level, which is somewhat challenging and requires homogeneous samples with a sharp transition. Measurements of the upper and lower critical fields, in contrast, are less demanding on the sample quality.

### Lower critical field $H_{c1}$

By definition, the magnetic field starts penetrating the sample at  $H_{c1}$ . Thus, magnetization measurements as a function of field at constant temperature are the usual way to determine  $H_{c1}(T)$ . Operationally,  $H_{c1}$  is taken where  $M(H)$  starts deviating from the linear  $M$ - $H$  relationship. Two points must be taken into account.

1. Corrections for the shape-dependent demagnetizing field must be included. When working with single crystals or very dense polycrystalline samples, this introduces only minor uncertainties of the order of  $\sim 5\%$ . A convenient self-consistency check is to compare the calculated and measured slopes of  $M(H)$ . In loosely compacted powder samples, the determination of the demagnetizing corrections is less straightforward because the true demagnetization factor cannot necessarily be calculated from the sample shape. We found it useful to measure  $M(H)$  for differently shaped samples, usually thin plates and bars with the field applied along the main geometrical axis.
2. Above  $H_{c1}$ , a time dependence of  $M$  is often observed which is associated with the dynamics of flux flow. Observation of this effect at a set field clearly means that  $H_{c1}$  has been exceeded, thus giving an upper limit of  $H_{c1}$ . Since flux flow (or creep) is always faster at higher temperatures,  $dH_{c1}/dT$  is reliably measured close to  $T_c$ , but slow penetration of flux might lead us to overestimate  $H_{c1}$  at low temperatures.

We measured  $H_{c1}$  on several samples of  $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$  (BPBO) which were grown at different times over the last six years and consistently found a slope  $H'_c$  near  $T_c$  of 1.8–2.5 Oe/K. Samples vary slightly in their  $H_{c2}$  slope (see next paragraph), which in turn reflects itself also in the  $H_{c1}$  slope. Two different magnetometers were used (S.H.E. 905, Quantum Design) and good agreement of the most recent



**Figure 1**

Magnetization of  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$  crystals to determine the upper critical field  $H_{c2}(T)$ . The curves are displaced for clarity. For a given field, the transition temperature is given by the deviation of  $M(H)$  from the constant value at higher temperature.

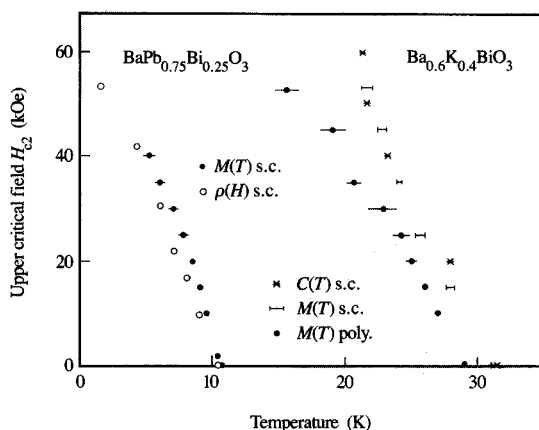
data with our older values [5] was found. For  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$  (BKBO),  $H'_{c1}$  is somewhat larger ( $4.5 \pm 0.5$  Oe/K) [6].

### Upper critical field $H_{c2}$

Traditionally, the upper critical fields are extracted from resistance measurements in a magnetic field. This procedure, however, is not applicable to cuprate-high- $T_c$  superconductors because of the intrinsic "broadening" of the resistive transition due to flux-motion-induced dissipation [7]. In the Bi-O-based superconductors, these effects are not obviously present. Alternatively,  $H_{c2}$  is measured magnetically. In a temperature sweep at constant field,  $H_{c2}$  is taken as the point where the magnetization starts deviating from the normal state value. In **Figure 1**, a typical result is shown with each curve shifted for clarity by an arbitrary amount.

For BPBO single crystals we have used both the resistive and magnetic methods to measure  $H_{c2}(T)$ ; examples for two crystals are shown in **Figure 2**. The slope close to  $T_c$  varies slightly from sample to sample, ranging from  $\sim 5.5$  to  $\sim 8.5$  kOe/K, most likely reflecting different resistivities. Previously reported values for  $H_{c2}$  fall within this range [5, 8, 9].

In the case of BKBO, we measured  $H_{c2}$  magnetically on both polycrystalline samples and single crystals. Several aspects are worth pointing out. First, the slopes for polycrystalline and single-crystal samples are the same



**Figure 2**

Upper critical field  $H_{c2}(T)$  of  $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$  and  $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ . Various techniques were used: magnetization  $M(T)$ , resistance  $\rho(H)$ , or specific heat,  $C(T)$  [11]. (s.c. = single crystal.)

**Table 1** Sommerfeld parameter  $\gamma$ , measured density of states  $N^*(0)$  and band structure density of states (from [16]). The range of the  $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$  values reflects both scatter among various crystals and experimental uncertainties.

|                                       | $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ | $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ |
|---------------------------------------|------------------------------------------------|---------------------------------------------|
| $\gamma$ (mJ/mole f.u. $\text{K}^2$ ) | $0.8 \pm 0.2$                                  | $\sim 1.5$                                  |
| $N^*(0)$ (states/eV f.u.)             | $0.34 \pm 0.09$                                | $\sim 0.64$                                 |
| $N(0)$ (states/eV f.u.)               | 0.24                                           | 0.42                                        |
| $\lambda$                             | $\leq 0.8$                                     | $\sim 0.5$                                  |

f.u. = formula unit.

despite the slightly different  $T_c$ . The upper critical field increases linearly with temperature near  $T_c$ , with a slope of  $\sim 5$  kOe/K. This is in contrast to an upward curvature reported in [10], where  $H_{c2}$  was extracted from resistance measurements on what appears to be nonhomogeneous material with nonmetallic  $R(T)$  characteristics. Thus, we conclude that magnetic measurements are better suited if phase inhomogeneity adversely affects resistive measurements. Finally, we mention the recent specific heat measurements on BKBO single crystals by Graebner et al. [11], where the anomaly at  $T_c$  has been followed in magnetic fields and, thus,  $H_{c2}(T)$  determined independently (see Figure 2). The agreement between the specific heat and the magnetic results on single crystals from the same preparation is excellent. While  $H_{c2}$  increases linearly near  $T_c$ , the single-crystal data suggest an upturn of  $H_{c2}$  below  $\sim 25$  K.

## Basic parameters

The main purpose of the critical field measurements is to calculate a few characteristic physical quantities. All derivations are based on standard expressions (see for example [12]). We note that these are extreme type-II superconductors with magnetic penetration lengths much larger than the coherence length. ( $\kappa \approx 100$  in BPBO,  $\approx 45$  in BKBO.) The large penetration length is due to the low carrier concentration measured to be  $n$ -type in BPBO (to  $2.5\text{--}4.5 \times 10^{21} \text{ cm}^{-3}$ , e.g., [8, 13]). For BKBO,  $p$ -type conduction was reported for polycrystalline material [14], and from the K concentration we would calculate  $4\text{--}5 \times 10^{22}$  electrons per cubic centimeter. The effective mass  $m^*/m_e$  for both superconductors is less than 1: 0.3–0.5 estimated for BPBO from experiments (see [9]), and  $\sim 0.5$  calculated [15]. In BKBO  $m^*$  was estimated from thermopower results to be about 0.15 [14]. The effective mass is so small because the Fermi level lies in a broad ( $\sim 16$  eV) band, derived from O  $2p$  and the (Pb,Bi)  $6s$  levels [16].

## Density of states and coupling strength

From the slope of the thermodynamic critical field  $H'_c$ , the specific heat anomaly  $\Delta C$  at  $T_c$  can be obtained from the well-known equation,  $\Delta C = VT_c H'^2/4\pi$ . This  $\Delta C$  is related to the Sommerfeld constant  $\gamma$  [and in turn to the electronic density of states  $N^*(0)$ ] through

$$\Delta C = f(\lambda) 1.43 \gamma T_c.$$

In the weak coupling limit ( $\lambda < 1$ ), the factor  $f(\lambda)$  is only slightly larger than 1 ( $\sim 1.05$  for  $\lambda \sim 0.8$ ), but is greater than 1 for intermediate to moderately strong coupling, and becomes less than 1 for very strong coupling. A recent extensive calculation of  $f(\lambda)$  for a class of coupling functions  $\alpha^2 F(\omega)$  can be found in [17].

For a first estimate of  $\gamma$  we use  $f(\gamma) = 1$ , which yields an upper bound for  $\gamma$  of  $0.8 \pm 0.2$  mJ/mole  $\text{K}^2$  for BPBO and  $\sim 1.5$  mJ/mole  $\text{K}^2$  for BKBO. In Table 1 the resulting density of states  $N^*(0)$  is shown with band structure calculation [16] values of  $N(0)$ . In the conversion of  $\gamma$  into  $N^*(0)$ , care must be exercised whether the density of states is defined per spin orientation. (The numerical values printed in [6] do not have this factor of 2 included, but the conclusions on  $\lambda$  are based on comparisons of the proper quantities and thus remain unchanged.) By comparing the experimental  $N^*(0) = (1 + \lambda)N(0)$  with the band structure values of  $N(0)$ , the coupling strength  $\lambda$  is found not to exceed 1. Somewhat larger values for  $\lambda$  were estimated previously for BPBO [5, 18]. The Bi–O superconductors are not in the strong coupling limit as measured by  $\lambda$ .

Although this main result may appear surprising in light of the high transition temperature, it is fully consistent with other measurements. Early tunneling results on high-quality junctions with negligible leakage current and only thermal broadening of the spectra gave a gap value  $2\Delta \approx 3.5 \pm 0.1$

[13]. A more recent study also found the same  $\Delta/T_c$  ratio when the measured  $T_c$  is used [19]. And finally, far-infrared spectroscopy also gave a gap of  $2\Delta \approx 3.2 kT_c$  [20]. All of these results are consistent with weak-to-intermediate coupling.

### $T_c$ compared to $N^*(0)$ : The $T_c$ - $\gamma$ plot

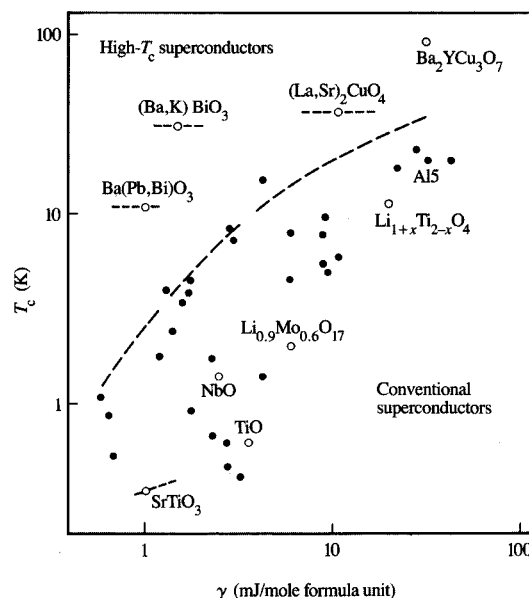
The uniqueness of BiO superconductors becomes evident when they are compared to other superconductors with similar density of states  $N^*(0)$ . For simplicity,  $T_c$  is plotted vs. the Sommerfeld constant  $\gamma$ , which is proportional to  $N^*(0)$  (see Figure 3). The basic reasoning behind such a plot is that higher density of states at  $E_F$  favors higher  $T_c$ , if the coupling strength and the boson frequency are kept constant. Among all superconductors, the bismuthates have the highest  $T_c/\gamma$  ratio and are properly called "high- $T_c$  superconductors."

It appears instructive to refer to the relative  $T_c/\gamma$  scale, in addition to the absolute value of  $T_c$ , when discussing high- $T_c$  superconductors. As we had pointed out after the discovery of  $\text{La}_2\text{CuO}_4$ -based superconductors, the cuprates also have an extraordinarily large  $T_c/\gamma$  ratio, and their high  $T_c$  is not due to a large density of states at  $E_F$ , unlike the A15 compounds [21]. We note in passing that the value of  $\gamma$  in the cuprates is less well known than in the bismuthates, mainly due to major conceptual and practical limitations in extracting  $\gamma$  from  $\Delta C$  at  $T_c$  (even when neglecting the experimental uncertainties). Thus, the  $\gamma$ 's shown for the cuprates might be subject to future modification.

### A generalized phase diagram

In the starting compound  $\text{BaBiO}_3$ , the valence charge disproportionates and creates inequivalent sites with unequal Bi-O bond lengths. This charge density wave might be seen as a consequence of the tendency of  $\text{Bi}^{\text{IV}}$  to disproportionate into  $\text{Bi}^{\text{III}}$  and  $\text{Bi}^{\text{V}}$ , which in turn can be traced back to the relative instability of  $s^1$  in the atom as it is measured in the ionization potentials. Optical spectroscopy revealed a CDW gap in  $\text{BaBiO}_3$  of  $\sim 1$  eV [22]. This gap is slightly reduced when Pb is substituted for Bi, and a pseudogap structure is still observed in the metallic region ( $\text{Pb}_{0.75}\text{Bi}_{0.25}$ ). First optical spectra were presented recently for  $(\text{Ba},\text{K})\text{BiO}_x$  films which indicate a reduction of the CDW gap with increasing K content [23].

The relative amplitudes of the CDW, at least of their commensurate component, can be deduced from crystallographically determined Bi-O bond lengths. Empirical relations exist between bond length and strength, and we shall use them first to calculate the differences between the inequivalent Bi sites. (We are aware of the different numerical parameters for Bi-O bond strength calculations, but this does not affect the conclusions below. We also refer to a recent review article [24] elaborating on the concepts of oxidation state, valent state, real charge, and



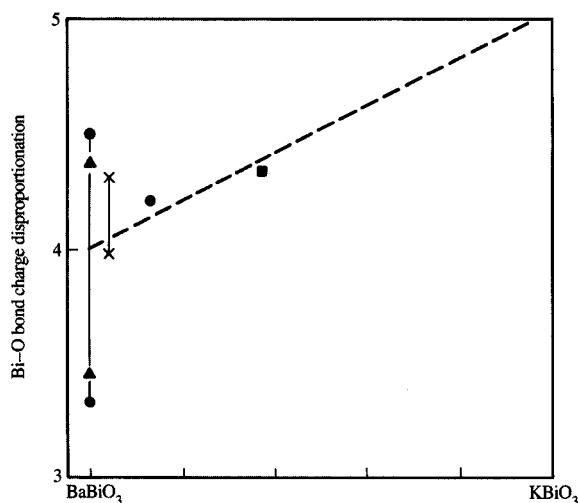
**Figure 3**

$T_c$  and Sommerfeld parameter  $\gamma$  for various superconductors. Among the oxides (open symbols), only the bismuthates and cuprates are high- $T_c$  superconductors.

chemical bond, particularly in the context of high- $T_c$  superconductors.)

The crystal structure of  $(\text{Ba},\text{K})\text{BiO}_3$  has been described in [25]. 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, confirming the original power diffraction results [1]. Thus, no bond charge disproportionation is present. A nonsuperconducting composition with  $\sim 4\%$  K crystallized in an orthorhombic structure with  $\text{CuO}_6$  octahedra having four short and two long Bi-O bonds alternating with octahedra having four long and two short bonds. The difference between the long and short bonds within an octahedron ( $\sim 0.11$  Å) is very pronounced and almost as large as it is between the "expanded" and "contracted" octahedra of  $\text{BaBiO}_3$  ( $\sim 0.13$  Å). Using the parameters from [26], we calculate the bond strength for the inequivalent Bi sites and find a difference of  $\sim 0.9$  for  $\text{BaBiO}_3$  and  $\sim 0.20$  for  $\text{Ba}_{0.96}\text{K}_{0.04}\text{BiO}_3$ . This is a crude measure of the commensurate CDW amplitude.

The distortions of the octahedra in  $\text{BaBiO}_3$  and  $\text{Ba}_{0.96}\text{K}_{0.04}\text{BiO}_3$  are notably different. Although we used the sum of the six bonds connecting Bi with O to calculate the bond strength, it might be equally interesting and probably more relevant to describe the structure in terms of short ( $s$ )



**Figure 4**

Average bismuth bond strength calculated from Bi-O bond lengths. In  $\text{BaBiO}_3$  and in  $(\text{Ba},\text{K})\text{BiO}_3$  with small K concentrations, two inequivalent Bi sites result from bond charge disproportionation. All Bi sites are equivalent in the  $\text{K}_{0.13}$  and  $\text{K}_{0.4}$  crystals. The expected bond strength is indicated by the broken line (see text for discussion).

and long (*l*) Bi-O bonds. This notation emphasizes *bond charges*, in contrast to charge localized on the Bi atoms. The  $\text{BaBiO}_3$  structure then gives rise to the following sequences, when starting at a Bi atom and proceeding in the *x*, *y*, and *z* directions: *lssl*, *lssl*, *lssl*. In the  $\text{K}_{0.04}$  compound, the sequence is *lssl*, *lssl*, *slls*. The two structures are thus mainly different through the *z*-direction modulation sequence: The bond charge density wave along *z* is shifted by one octahedron.

Returning to the total bond strength, we have plotted it for the various K concentrations in **Figure 4**. Starting at  $\text{BaBiO}_3$ , the average bond strength is close to 4, with a site difference of  $\sim 0.9$ . With progressively higher K content, the average bond strength increases, roughly following the broken line, which is what one expects from simple valence considerations ( $\text{KBiO}_3$  is not a perovskite). The Bi-O bond lengths become equal for all Bi sites at  $\sim 10\%$  K substitution, and a crystal with  $\sim 13\%$  K was found to be simple cubic but not superconducting [27].

A generalized phase diagram for  $(\text{Ba},\text{K})\text{BiO}_3$  and  $\text{Ba}(\text{Pb},\text{Bi})\text{O}_3$  is shown in **Figure 5**. Starting from the charge-disproportionated end member  $\text{BaBiO}_3$ , the CDW state persists until about 20–40% of Ba is replaced by K. The precise location of the boundary is not clear, because of

problems with material preparation and chemical analysis. The broken line is thus not established in all details [1, 28]. When substituting on the electronically active B sublattice, the CDW state persists over a wider range to a composition of  $\text{Bi}_{0.3}\text{Pb}_{0.7}$ . In both cases a CDW is formed when the antibonding *s-p* band is half and slightly less than half filled. The highest  $T_c$  is observed in the metallic range close to the CDW border. One might expect  $T_c$ 's well in excess of 30–35 K if the metallic state could be stabilized more closely to half filling, i.e., with less substitution. One reason is simply that the band density of states increases toward half filling [16].

The main features of this phase diagram have been discussed theoretically by several authors [29–31]. Emphasis is put on the electron-lattice interaction, the tendency to real-space pairing of electrons, and the intrinsic instability of  $\text{Bi}^{\text{IV}}$  toward disproportionation. A theoretical phase diagram based on the latter approach [31] has the generic features of **Figure 5**.

### Comparison with Cu-O superconductors

It appears worthwhile to point out several basic similarities between the Bi-O and Cu-O superconductors. First, their bonding and electronic structure are quite unique among all oxide superconductors. The oxygen 2*p* orbitals are strongly hybridized with the central metal atom (Bi 6*s*, Cu 3*d*) states. This is essentially element- and structure-specific in that the atomic 6*s*/3*d* levels, after renormalization by the Madelung potential, end up energetically close to the oxygen 2*p* states. This, together with a large mixing matrix element, leads to a broad band of bonding character in the lower part and antibonding in the upper. Nonbonding O 2*p* states form a rather narrow band manifold.

Characteristic for both the Cu-O and Bi-O compounds is the location of the Fermi level in the upper part of this broad band. In the end members,  $\text{LaCu}_2\text{O}_4$  and  $\text{BaBiO}_3$ , the "antibonding" band is half filled, and thus metallic behavior might be expected in the absence of instabilities. The unoccupied uppermost part of this band has significant O 2*p* character. The presence of these *p* holes is characteristic for the Bi-O and Cu-O superconductors and sets them apart from all the other oxide superconductors, where the O 2*p* states are all filled and located well below the Fermi level, which lies in *d*-derived conduction bands, e.g., in  $\text{SrTiO}_3$ , in  $\text{M}_x\text{WO}_3$ , or in  $\text{LiTi}_2\text{O}_4$ . (See, e.g., [32] and references therein.) The  $T_c$ - $\gamma$  plot reflects this distinct difference between the "high- $T_c$ " and "low- $T_c$ " oxides.

While the pairing mechanism in the Bi-O and Cu-O superconductors is not yet identified, it appears to us that they have so much in common, both phenomenologically and crystal-chemically, that the same mechanism might lead to high- $T_c$  superconductivity. If such a unified picture were appropriate, it would not be a magnetic mechanism, as the bismuthates are not magnetic. Besides the phonon mechanism, the charge excitation models might apply to

both cuprates and bismuthates. Finally, we note the observation of sizable oxygen isotope effects in the bismuthates and also in the  $(\text{La}, X)_2\text{CuO}_4$  [6, 33–35]. These results might be interpreted as evidence for an exclusively phononic mechanism, but a combination of phononic and, e.g., another “higher-frequency” mechanism would still produce an isotope effect [36, 37]. We speculated that even a pure charge-transfer excitation mechanism could lead to a “parasitic” isotope effect [6].

## Summary

We have reviewed the measurements on the  $(\text{Ba}, \text{K})\text{BiO}_3$  and  $\text{Ba}(\text{Pb}, \text{Bi})\text{O}_3$  superconductors from which the density of states and  $E_F$  can be derived. Comparing these values with band structure calculations, we find that Bi–O superconductors are not in the strong coupling regime. These compounds are clearly high- $T_c$  superconductors in that the  $T_c/N^*(0)$  ratio is high. Cuprates and bismuthates share common basic features of the electronic structure and are distinctly different from other oxide superconductors.

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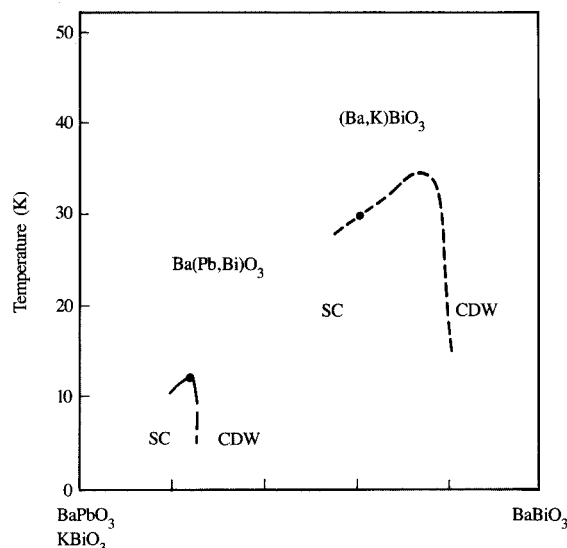


Figure 5

A generalized phase diagram for  $(\text{Ba}, \text{K})\text{BiO}_3$  and  $\text{Ba}(\text{Pb}, \text{Bi})\text{O}_3$ . In each system, the highest  $T_c$  is observed close to the border with the semiconducting CDW state. The precise location of the SC–CDW boundary is not known for BKBO, and the details of the broken lines remain to be explored in detail. It is also questionable whether the Pb–Bi and Ba–K ratios can be changed continuously.

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