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PHYSICA

Analysis of superconductivity in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ on the basis of indirect-exchange mediated pairing

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Abstract

After a critical survey of current interpretations of superconductivity in $(\text{Ba,K})\text{BiO}_3$, we present a quantitative analysis of this system, with emphasis on dependence of the critical temperature on potassium content and on pressure (external or ‘chemical’). Adopting a BCS formalism, Cooper-pair formation is assumed not to be phonon-mediated, but to arise from indirect-exchange interactions between conduction electrons via oxygen anions (oxygen valence band), by analogy with previous analyses of cuprate high- T_C superconductors. Numerical calculations are carried through with, and without, accounting for shrinkage of the lattice with increasing potassium content. Results for pressure gradients of T_C , at varying doping, and T_C under pressures up to 20 GPa, are compared with experimental data. Extension of the analysis to the bismuthate $\text{Ba}(\text{Pb,Bi})\text{O}_3$ is outlined.

1. Introduction. Survey of existing analyses

1.1. Superconductivity in the bismuthates

The discovery in 1988 [1] of superconductivity in the strictly 3-dimensional perovskite $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with a highest critical temperature of ≈ 30 K at $x \approx 0.40$ (about the same T_C as for the first high-temperature cuprate $\text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4$, and not much lower than $T_C = 39$ K of its Sr substitute) invalidated the up-to-then prevalent belief that (quasi-) two-dimensional oxide layers containing Cu are a necessary condition for T_C values beyond 30 K. In addition, this high T_C was attained in spite of a very low density-of-states $N(E_F)$ on the order of 10^{-1} states/(eV. spin.cell), considerably lower than that of A15 alloys such as Nb_3Sn with a lower critical temperature (23 K). Interest in the bismuthates had been aroused by the earlier (1975) finding that

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the related perovskite $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ exhibits superconductivity with a maximum T_C of 13 K, at $x \approx 0.25$ [2], high among superconductors containing no transition element. Many efforts have since these discoveries been undertaken towards elucidating the pairing mechanism responsible for such unexpected behavior. Excellent reviews can be found a.o. in papers by Boyce et al. [3], Hamada et al. [4] and, more recently, by Namatame et al. [5, 6]. We will first consider properties of $(\text{Ba}, \text{K}) \text{BiO}_3$, usually abbreviated BKBO, together with $\text{Ba}(\text{Pb}, \text{Bi}) \text{O}_3$ or BPBO, and later concentrate on BKBO as a member of the ‘high- T_C ’ family ($T_C \geq 30$ K). A number of structural properties are mentioned first, primarily taken from a detailed neutron-diffraction analysis by Pei et al. [7].

1.2. Structural properties of BKBO and BPBO

$\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ (BKBO) has a complex phase diagram [7]. For a K-doping concentration $x < 0.1$ its structure is body-centered monoclinic. At higher doping, the crystal is orthorhombic until $x = 0.37$, and then goes over into an essentially undistorted cubic configuration, until at $x = 0.50$ the potassium solubility limit is reached. The superconducting phase is thus the undistorted cubic structure. (Some evidence [7] points to the possible occurrence of a tetragonal phase between orthorhombic and cubic.) Starting with the latter, the different non-cubic structures can be described in terms of a sequence of first a tilting of BiO_6 octahedra, and then accompanied by oxygen breathing-mode distortions (monoclinic phase) upon decreasing the potassium content x . This results in (alternating) inequivalent Bi sites because of oxygen atoms displaced (‘frozen’) toward or away from the Bi atoms. From neutron-diffraction and EXAFS (extended X-ray absorption fine-structure spectroscopy) studies the two Bi-O distances were found to be approximately 2.29 and 2.11 Å. The observed difference led to an interpretation in terms of a valence disproportionation $\text{Ba}_2(\text{Bi}^{3+}, \text{Bi}^{5+}) \text{O}_6$, reflecting the known diamagnetism of BaBiO_3 (instead of a magnetic state Bi^{4+} with one 6s-electron). The frozen oxygen breathing mode can then be viewed as the origin of a long-range charge-density wave (CDW) in this material, with concomitant semiconducting behavior. For the orthorhombic phase, Pei et al. [7] detected *only* tilting, *no* breathing distortions, i.e. the static CDW has disappeared and therewith the inequivalence of Bi sites. However, the orthorhombic material is a semiconductor; this poses a problem, since tilting alone cannot be expected to destroy metallicity of the undistorted cubic phase. Instead, it has been suggested [4, 7] that in the orthorhombic phase the degree of ordering of ‘ Bi^{3+} ’ and ‘ Bi^{5+} ’ is continuously reduced by increased K doping, i.e. the monoclinic-orthorhombic transition is of order-disorder type. The disordered phase would have the same breathing-type distortion, but only on a local (or dynamical) scale. Also for the superconducting phase of BKBO there is some evidence [4] that two different Bi-O distances *continue to exist*. It should be emphasized that in this framework the assignment ‘ Bi^{3+} ’, ‘ Bi^{5+} ’ is certainly too radical a notation; it only indicates different types of Bi-O bonding in the bismuthates. Details on the transition between metallic

(cubic phase) and semiconducting (orthorhombic phase) proposed from photoemission spectra, involving the formation of a ‘pseudogap’ at E_F upon increased doping, are found in Ref. [5].

The structure of $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ (BPBO) is orthorhombic for $x < 0.1$ and $0.35 < x < 0.9$, tetragonal for $0.1 < x < 0.35$ and monoclinic for $x > 0.9$ [5, 7]. The phases up to $x = 0.35$ are metallic (BaPbO_3 is a semimetal); beyond that limit they are semiconducting. The tetragonal configuration carries the superconducting phase, with maximum $T_C = 13$ K at $x = 0.25$. It is noteworthy that it takes $1 - x = 0.65$ in Pb concentration to render BaBiO_3 metallic, against only $x = 0.35$ in K for BKBO. EXAFS studies of BPBO have identified [3] two Bi-O bond lengths over the whole spectrum of x , thus also in the superconducting phase¹. The difference increases somewhat with increasing x (Bi doping). We note that in both BKBO and BPBO the lattice distortions in the non-cubic phases are sufficiently small for using a ‘pseudo-cubic lattice’ in all phases.

The above results indicate that, in both BKBO and BPBO, Bi tends to maintain the same oxygen environment, including the variation in Bi-O bond lengths, as it possesses in the reference compound BaBiO_3 .

1.3. Interpretations of superconductivity in (Ba,K) BiO_3

We now concentrate on BKBO and review present understanding of superconductivity in this system. Pei et al. [7] determined T_C for different K doping, finding that superconductivity suddenly appears at x only slightly below 0.37, i.e. at the semiconducting (orthorhombic)-to-metallic (cubic) transition. Starting from the (practically) highest value of T_C measured along the curve, T_C rapidly decreases to about 20 K at the potassium solubility limit $x = 0.50$. Photoemission studies [5] show that with increasing x the spectra are shifted towards the Fermi level, indicating a decrease of E_F with increased hole doping. However, the magnitude of the shift is considerably smaller than that predicted by band-structure analyses [4, 8]. These calculations are based on an assumed rigid-band emptying of the conduction band with K doping (‘hole count’), which apparently is too simple an interpretation. From their neutron-diffraction studies, Pei et al. [7] find that the lattice shrinks somewhat, as $a = 4.3548 - 0.1743x$, with a the pseudo-cubic lattice parameter, which could imply an increased (formal) charge on Bi sites (the radii of K^+ and Ba^{2+} are practically identical). A joint effect of E_F lowering and lattice shrinking might explain the discrepancy between band-structure results and photoemission shifts.

An *essential* difference between high- T_C cuprates and the bismuthates is that in the cuprates, (cation) hole doping leads to the formation of *new states* (or doping-induced

¹Existence of two Bi-O distances in the superconducting phase (breathing-type local lattice distortions) of BPBO is still controversial; they were not detected through photoemission analyses. Detailed references are given in Ref. [5].

shift of spectral weight) which appear close to E_F in the charge-transfer gap of the parent compounds (see, e.g. [9–11]). In BKBO (or BPBO) this phenomenon does not (or scarcely) occur. As we will discuss, this distinction implies a different interpretation of T_C as a function of doping, and pressure, between the two categories of superconductors.

Turning to the possible pairing mechanism in (Ba,K) BiO₃, it is clear from the absence of local magnetic moments that magnetically mediated pairing can be excluded. In fact, there are strong indications that the superconductivity can be treated in the BCS framework of (weak-to-) moderate, s-wave, coupling. Among several experiments we mention a very recent determination of the energy gap as a function of temperature from tunneling data by Szabó et al. [12]. The maximum T_C was 32 K; $\Delta(T)$ was found to closely follow the BCS prediction with $\Delta(0) \approx 3.5$ meV, taking into account a ‘smearing factor’ of 0.5 meV in the spectra. The reduced gap $2\Delta(0)/k_B T_C$ amounts to 4–4.3, indicating a medium coupling strength. Measured values of the London penetration depth, as a function of temperature, by Ansaldo et al. [13] using muon spin-rotation relaxation (μ SR) on a sample with $T_C = 26$ K, showed good agreement with BCS weak coupling. At the lowest T the penetration depth was found to be 3400 Å. Very similar (microwave) results were recently obtained by Pambianchi et al. [14], leading to a somewhat reduced gap of 3.8 ± 0.5 . No results available on BKBO, known to us, imply a serious challenge of a BCS s-wave classification of superconductivity in BKBO (this applies to BPBO as well).

Identification of the *mechanism* of Cooper-pair formation in the bismuthates, on the other hand, turns out to be a much more complex problem. Measurements of the *isotope effect* on T_C from ¹⁸O substitution for ¹⁶O led to values of the isotope coefficient $\alpha \equiv -\text{dln}T_C/\text{dln}M_O$ (M_O is the oxygen mass) of 0.21 ± 0.03 by Batlogg et al. [15], 0.35 ± 0.05 by Kondoh et al. [16] and 0.41 ± 0.03 by Hinks et al. [17]. As Hellman [18] has pointed out, the differences in α may in part be due to different isotope fractions in the samples used ($96 \pm 3\%$ in [17]; lower in the others). In any case, a sizable isotope effect naturally leads to the supposition that phonon-induced pairing is a primary contributor to Cooper-pair formation. However, this interpretation may well be too simple. From an analysis of experimentally observed large values and rapid variation of the oxygen isotope coefficient upon doping in cuprates, Carbotte and Akis [19] demonstrate that such effects can be (qualitatively) understood in terms of a predominantly *electronic* pairing mechanism with only a relatively small electron-phonon contribution. Consequently, sizable values of the isotope coefficient need not imply a dominant electron-phonon contribution to the pairing.

More pertinent information on the pairing mechanism is obtained from the analysis of *tunneling spectra*. Several high-resolution tunneling experiments have been carried out on (Ba,K) BiO₃, starting with Zasadzinski et al. [20, 21], who used an oxide layer as surface tunnel barrier and an indium thin-film counterelectrode. Two principal parameters for superconductivity can be deduced from the measured current-voltage

tunneling function $I(V)$, in particular from its first (conductance (dI/dV)) and second (d^2I/dV^2) derivatives. These are the Eliashberg spectral function $\alpha^2F(\omega)$ with α a matrix element measuring the coupling strength of the electrons to phonon (boson) modes of energy $\hbar\omega$, and the Coulomb repulsion parameter μ^* , which occur in the Eliashberg gap integral equations. This information is extracted from $I(V)$ through an inversion iterative process developed by McMillan and Rowell [22] for low- T_C metals and alloys. Ideally, the conductance dI/dV in the superconducting state shows a sharp peak at the voltage $V = \pm \Delta/e$. It should be emphasized here that this procedure applies for *general* boson-mediated pairing, but we restrict ourselves to phonon coupling as it is applied in the literature.

In the ideal case, when detailed (and sample-independent) experimental information from tunneling is available concerning $\alpha^2F(\omega)$ and μ^* , or else can be obtained theoretically, then the coupling strength λ is calculated by integrating $2\alpha^2F(\omega)/\omega$ over the (phonon) spectrum. Together with μ^* , the equation for the gap is then readily solvable on a computer, and the critical temperature T_C follows automatically. If such is not the case, then we have to use an estimated value, or an approximated (see below) expression for λ and ‘reasonable’ values of μ^* to be inserted into a McMillan- or (strong-coupling) Allen-Dynes-type of ‘approximate T_C -equation’ deduced semi-empirically for low- T_C materials. It is essential to note that such an *ad hoc* procedure may severely obscure the reliability of calculated values for other properties, such as pressure, or doping, dependence of T_C . For details on the McMillan–Rowell inversion procedure we refer to the literature [22,23].

A critical test of the assumed phonon-mediated coupling lies in a comparison of $\alpha^2F(\omega)$ with the *phonon* spectrum (density-of-states) $F(\omega)$ of the system. Although the parameter α may depend on ω , i.e. the shape of $\alpha^2F(\omega)$ may be different from that of $F(\omega)$, basic features such as peaks and valleys in the two functions should occur at nearly the same energies. Whereas for low- T_C superconductors there generally exists a *striking* resemblance between $\alpha^2F(\omega)$ and the phonon density-of-states, e.g. in Pb [22,23], the situation is much more complicated with high- T_C materials, including (Ba,K) BiO₃. A detailed determination of the phonon spectrum of this system, doped and undoped, was obtained with inelastic neutron scattering (INS) together with molecular dynamics simulations by Loong et al. [24]. From changes in the phonon spectrum at superconducting compositions it was inferred that ‘the coupling of electrons to 30- and 60-meV oxygen phonons is responsible for superconductivity in Ba_{0.6}K_{0.4}BiO₃’.

A comparison between $F(\omega)$ and the spectral function $\alpha^2F(\omega)$ deduced from tunneling data by Huang et al. [25], and Samuely et al. [26] shows that, although there is some correspondence between characteristic features, the striking resemblance obtained with low- T_C systems is no longer observed. In addition, the detailed shape of $\alpha^2F(\omega)$ turns out to be rather *sample* dependent. Consequently, an unambiguous determination of (especially) the coupling strength λ for (Ba,K) BiO₃ cannot be made. Samuely et al. [26] have given a detailed account of experimental complexities and reproducibility of tunneling results. We refer to that paper for more insight into the

potential of tunneling experiments. Values of the gap, the coupling parameter λ and the Coulomb parameter μ^* deduced from inversion analyses vary between (Δ) 3.8–5.0 meV, (λ) 0.7–1.3, and (μ^*) 0–0.11 [25, 26]; the reduced gap $2\Delta/k_B T_C$ amounts to 3.8–4.1, indicating medium-strong coupling.

1.4. Direct calculations of parameters

In addition to results deduced from tunneling experiments, values of the superconductor parameters, primarily the coupling strength λ , have been evaluated theoretically in a number of papers. In a first analysis, on $\text{Ba}_{0.71}\text{K}_{0.29}\text{BiO}_3$ of assumed cubic symmetry, Hamada et al. [4] carried through a band-structure calculation on the basis of the so-called FLAPW (full-potential linearized augmented plane wave) method in the local density approximation. The results are very similar to those reported earlier by Mattheiss and Hamann [28] using a self-consistent LAPW basis: just one antibonding (Bi6s–O2p) band crosses the Fermi level. The Fermi surface at $x = 0.29$ is rather free-electron like; variable doping is treated adopting a rigid-band approximation.

To evaluate the electron-phonon coupling, the authors of [4] computed λ as $\lambda = \sum_j (\eta_j / M_j \langle \omega^2 \rangle)$, where the η_j are so-called McMillan–Hopfield parameters each containing the squares of electron-phonon matrix elements for vibration modes of atom j with atomic mass M_j , and where $\langle \omega^2 \rangle$ is a Fermi surface average. For a Debye phonon spectrum $\langle \omega^2 \rangle = \frac{1}{2} \theta_D^2$ (θ_D is the Debye temperature). The parameters η_j were determined using the rigid-muffin-tin approximation of Gaspari and Gyorffy [27]; the resulting values are $\eta_{Ba} = 0$, $\eta_{Bi} = 0.07$ and $\eta_O = 1.71$ (in units eV/Å²), i.e. the electron-phonon coupling is predominantly due to oxygen phonon modes, as expected. From a knowledge of η_j and with $\theta_D = 200$ K while choosing $\mu^* = 0.1$, the McMillan equation yields $T_C \approx 30$ K. However, this good agreement cannot be accepted since the corresponding value of the coupling λ is 3.0, outside the range of applicability of the McMillan formula.

An extensive analysis of electron-phonon coupling and superconductivity in both (Ba,K) BiO₃ and Ba(Pb,Bi) O₃ was carried through by Shirai et al. [29], approximating the conduction-band states of [28] by a tight-binding representation with three kinds of Slater-Koster transfer integrals. To determine phonon spectra, force constants were fitted to observed frequencies in $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$, and transferred unchanged to (Ba,K) BiO₃. A frozen oxygen breathing mode, for (K,Pb) doping ≤ 0.1 , was introduced *ad hoc* by choosing the space derivatives of the transfer integrals such as to make this mode vanish, rendering the cubic structure unstable against distortion (formation of a static charge-density wave). Critical temperatures as a function of doping level were calculated directly from the (linearized) Eliashberg equations, assuming different values for the parameter μ^* . For all details we refer to the authors' original paper [29].

The results of the analysis are remarkable indeed. Upon comparing the functions $F(\omega)$ and $\alpha^2 F(\omega)$ it is found that their frequency dependence is *entirely different*, which

is surprising in view of the tunneling results [25, 26]. With decreasing (K,Pb) doping, $\alpha^2 F(\omega)$ shifts markedly to lower frequencies and develops more intensity, especially in the range 20–40 meV, whereas the phonon density-of-states $F(\omega)$ is much less sensitive. The shift to lower frequencies and increase of $\alpha^2 F(\omega)$ lead to a *rapid increase* of the electron-phonon coupling λ at lower doping levels, reaching a value of about 1.5 for fractional (K,Pb) doping slightly larger than 0.1, whereas at 0.4 doping λ is about 0.8, rather close to the tunneling results. The critical temperatures T_C , in turn, reach values in excess of 35 K at a level of 0.2 (K or Pb), about 20–30 K at fraction 0.4, in relatively good agreement with experiment, but they are very sensitive to chosen values of μ^* between 0 and 0.15. There is *no maximum* of T_C for varying (K,Pb) doping.

Whereas these results are somewhat reasonable for K-doped BaBiO₃, the Pb-doped systems are poorly represented by the theory: at 0.75 Pb content λ is only slightly above 0.20 and T_C reaches no more than a few K (exp. 13 K). The conclusion must be that in any case Ba(Pb,Bi)O₃ cannot be described by this type of analysis. In an earlier paper [30] along the same lines, the authors concentrated on Ba(Pb,Bi)O₃ while adopting lower values (by about 30%) for the space derivatives of the three transfer integrals. The critical temperatures are now very much higher, reaching 18 K at 0.7 Pb doping, again without the experimentally observed maximum in that range. A major extension of these tight-binding calculations, including a detailed analysis of crystal-field matrix elements and their dependence on doping, has recently been undertaken by Vielsack [31]. The results are similar to those of Shirai et al. [29]. Again, this type of analysis appears not to apply to Ba(Pb,Bi)O₃ [32].

We finally note that in these analyses no CDW (long-range, local or dynamical) is assumed to exist outside the monoclinic range (< 0.1 doping) for (Ba,K) BiO₃. Consequently, the semiconducting property of the orthorhombic phase remains unexplained. Nevertheless, these calculations are of great value in demonstrating, assuming phonon-mediated pairing, what can be achieved on a first-principle theoretical basis.

In an analysis by Liechtenstein et al. [33] the total (static) lattice energy of Ba_{1-x}K_xBiO₃ was calculated for undoped and 0.5 K-doped BaBiO₃ as a function of tilting and breathing distortions. The band-structure calculation was based on a FLMT0 (full-potential linearized muffin-tin orbital) method in the local density approximation, including a small set of atomic functions, originally developed by Methfessel et al. [34] in the analysis of structural and dynamical properties of Si in the diamond structure. A characteristic result of the application to Si is that the lattice constant and bulk modulus are very well reproduced, whereas the cohesive energy is overestimated, by as much as 13%, a well-known general failure of the local density approximation. The authors of [33], nevertheless, strikingly reproduce an instability of the cubic lattice for undoped BaBiO₃ against both breathing and tilting distortions, implying a lowering of the lattice energy in the mRy range, i.e. of order 1 kcal/mole, whereas at 0.5 potassium doping both instabilities have vanished. The calculated dependence of the phonon coupling λ on doping is similar to that found by Shirai et al.

[29]. Once again, semiconductivity of the orthorhombic phase of $(\text{Ba},\text{K})\text{BiO}_3$ is not accounted for in this analysis.

A similar FLMTO total-energy analysis, for undoped BaBiO_3 , was carried through by Kunc et al. [35]. It should be noted that the calculated instability of the oxygen breathing and tilting modes is here *not* a consequence of nesting properties of the Fermi surface deduced from band-structure calculations on BaBiO_3 [36] (i.e. the observed distortion is not of the Peierls type). Neither in total-energy nor in band-structure analyses is there any indication of appreciable charge disproportionation at the Bi sites.

An analysis of enhanced superconductivity due to strong softening (renormalization) of oxygen breathing modes near the CDW instability, as a result of electron-phonon interaction, was earlier presented by Ting et al. [61]. The calculated coupling strength, and average phonon frequency, when inserted into an Allen–Dynes T_C -equation (assuming $\mu^* = 0$) yield a steep increase of T_C as the potassium doping level is lowered towards the CDW stability limit. Other, more qualitative, interpretations of superconductivity in the bismuthates are based on the general concept of *local* electron pairing (real-space pair formation), developed in particular by Micnas et al. [37]. This phenomenon can theoretically be incorporated in an extended Hubbard model in terms of a ‘negative- U ’ parameter at Bi sites. Rice [38] advanced the idea of a lattice ordering, in undoped BaBiO_3 , of bipolarons (or local two-electron pairs) on alternating Bi sites, stabilized by the strong relaxation of surrounding oxygen octahedra. Potassium doping would render these pairs mobile, thus destroying the local charge disproportionation at the Bi lattice points. In an early version, a local $(6s^2)$ pair on Bi^{3+} was thought to correspond to the chemical concept of ‘lone-pair’ electrons [39]. No concrete results have as yet emerged from such an interpretation.

1.5. Pressure coefficient of T_C in $(\text{Ba}, \text{K})\text{BiO}_3$ and $\text{Ba}(\text{Pb}, \text{Bi})\text{O}_3$

All since the discovery of high- T_C cuprate superconductivity, pressure effects on T_C have provided important experimental information concerning the pairing mechanism(s) in these materials [40]. For hole-doped cuprates, dT_C/dP is generally positive with a rough average of order 1 K/GPa, whereas electron-doped cuprates show negative dT_C/dP slopes of somewhat smaller magnitude [41]. A comparison between pressure effects in cuprates and bismuthates may thus be expected to provide a lead concerning similarities, or differences, between pairing mechanisms in the two categories of superconductors.

Chu et al. [42] measured dT_C/dP in $\text{Ba}_{0.9}\text{K}_{0.1}\text{Pb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ shortly after its discovery, obtaining $dT_C/dP = -(0.29 \pm 0.02)$ K/GPa (onset $T_C = 11.73$ K), of the *same* sign and magnitude as in electron-doped cuprates. The first pressure experiments on $(\text{Ba}, \text{K})\text{BiO}_3$ were carried out by Schirber et al. [43] on samples with $T_C = 16, 23$, and 25 K. The resulting dT_C/dP values are *positive* and of order 1 K/GPa ($T_C = 16$ K; half this value at $T_C = 25$ K), of the *same* sign and magnitude as in hole-doped cuprates. Recently, Beille et al. [44] measured $dT_C/dP = 0.38$ K/GPa

on a single crystal of (Ba, K) BiO₃ with $T_C = 31.5$ K, i.e. in the same range as Ref. [43]. These findings show that Ba(Pb, Bi) O₃ under pressure behaves like an *electron*-doped cuprate, (Ba, K) BiO₃ like a *hole*-doped cuprate. This is an *important lead* in the search for the pairing mechanism in the bismuthates, since with high- T_C cuprates an explanation of pressure effects on the basis of phonon-mediated pairing lies virtually outside the range of realistic possibilities [40, 41]. A recent attempt along those lines, with reference to YBa₂Cu₃O_y, has been presented by Neumeier [45].

1.6. Summary

In the preceding paragraphs we analyzed different aspects of superconductivity in the bismuthates, and we critically reviewed present interpretations of Cooper-pair formation in these systems, especially in (Ba, K)BiO₃. Of the various mechanisms proposed in the literature, phonon-mediated coupling has come closest to experimental verification. The following facts, however, speak *against* such a pairing mechanism:

(1) The pressure gradient, dT_C/dP , of the transition temperature, positive in (Ba, K) BiO₃, negative in Ba(Pb, Bi) O₃, and its close resemblance with hole- and electron-doped cuprates, respectively, *cannot* be reproduced on the basis of phonon-mediated coupling;

(2) The transition temperature as a function of doping, $T_C(x)$, in Ba_{1-x}K_xBiO₃ shows a highest value for x close to 0.37 [7], while T_C in BaPb_{1-x}Bi_xO₃ has its maximum at $x = 0.25$ [2], well inside the experimental range. Although with (Ba, K) BiO₃ experiments do not conclusively demonstrate a maximum of T_C in the physical range of x , the expected similarity between the two bismuthates renders a different interpretation of the $T_C(x)$ curve near $x = 0.37$ very unlikely. First-principle electron-phonon calculations [29–32] for either bismuthate show *no sign* of a maximum in T_C with doping;

(3) Assumed validity of the electron-phonon mechanism of pairing is based on the observation of isotope effects, and on the interpretation of tunneling experiments. Whereas isotope effects are generally no *direct* measure of phonon involvement in superconductivity (see e.g. [19]), the *uniqueness* of a (supposedly close) correspondence between the Eliashberg spectral function $\alpha^2F(\omega)$ and the phonon density-of-states is experimentally difficult to demonstrate [25, 26]. *Ab initio* calculations show little sign of such a relation [29, 30]. Batlogg et al. [15] speculated already shortly after the discovery of superconducting (Ba, K)BiO₃ that the involvement of phonons in bismuthate superconductivity might be ‘parasitic’, merely indicative of phonon-dressed *electronic* excitations mediating Cooper-pair formation.

In the following analysis we adopt an approach in terms of an electronic pairing mechanism in which Cooper pairs are formed through indirect exchange between conduction electrons via closed-shell oxygen anions (a full oxygen valence band). On this basis we have earlier analyzed superconductivity in the cuprates, in particular the

effect of doping and of pressure on critical temperatures [47–49, 52, 54], as well as superconductivity in alkali-doped fullerenes [50, 51]. In the next Section we summarize the main aspects of the indirect-exchange approach to high- T_C superconductivity, referring for details to the literature mentioned.

2. Indirect-exchange pairing in superconductors

2.1. Formalism

In the indirect-exchange approach [46–48] adopted we subdivide the electron states of the system considered into Fermi-liquid conduction states, to be treated in an effective-mass approximation, and doubly-occupied (thus diamagnetic) ‘core states’. In the cuprates and bismuthates, the latter represent the oxygen valence band. We select two conduction electrons with opposite wavevectors and spins, which form a Cooper pair in the superconducting phase.

The next step consists in formally solving Schrödinger equations for the two non-interacting conduction electrons on one hand, and the many-electron assembly of core electrons on the other hand, in the average (Coulomb) field of all other charges. Note that the eigenfunctions of the two subsystems are mutually *not orthogonal*, since they satisfy different eigenvalue equations. A configuration-interaction calculation is then carried out, again formally, in a product basis of these eigenfunctions fully antisymmetrized with respect to all (conduction-plus-core) electrons, with the core eigenfunctions restricted to the ground state.

We emphasize that the indirect-exchange interaction in the present approach is *directly* a consequence of enhanced permutation symmetry in joining the subsystems of conduction (Fermi-liquid) states and core states. This effect is *missing* in (*one-electron*) *band-structure calculations*.

As can be shown [46–48], the expression for the off-diagonal scattering-matrix element V_{qk} in the BCS reduced Hamiltonian then contains a direct term (i.e. without core interference) plus a contribution due to permutations of core- and conduction-electron labels. To simplify the terminology, the sum of these two terms is denoted as ‘indirect-exchange interaction’ between the two conduction electrons. Full details are given in the original paper [46] and in subsequent publications.

The method was originally developed for simple metals [46] and later extended to high- T_C cuprates [47, 48]. The effects of doping, and of pressure, on critical temperatures in cuprates were analyzed in [49], with a recent extension to the new Hg-cuprates where T_C reaches 160 K under high pressure [52]. Further generalization indicates that in alkali-doped C_{60} , carbon-carbon double bonds can mediate pair formation [50, 51], whereas in organic superconductors of the (BEDT-TTF) type, sulphur or selenium atoms may fulfill this role [53].

In view of the short-range character of exchange interactions, the valence-band oxygen states in cuprates and bismuthates are transformed to Wannier functions

centered at the oxygen sites, representing closed-shell (diamagnetic) units ('cores'). Applying this formalism, the critical temperature T_C is obtained in the form [46,48]

$$T_C = \langle A\omega \rangle \exp(-1/|W|), \quad \text{for } W < 0, \quad (1)$$

where $\langle A\omega \rangle$ is a characteristic temperature for the indirect-exchange coupling; $\langle A\omega \rangle$ is taken proportional to the Fermi energy of the conduction electrons. The parameter $|W|$ is the coupling strength, defined [46,48] as a function of V_{qk} in the vicinity of the Fermi surface, and of the density-of-states in an effective-mass approximation (electron band mass m^*). For small Fermi vector k_F we assume an isotropic band and we use the symbol k_F to denote $|k_F|$. In the application to cuprate superconductivity it was found [47,48] that for Tl_2 -cuprates with $N = 1, 2$, and 3 CuO_2 layers per molecular unit, taking T_C for $N = 1$ as *gauge point* in the procedure, (maximum) critical temperatures are reproduced with $\langle A\omega \rangle \approx 200$ K.

In the original paper [46] the formalism leading to an algebraic expression for the coupling W was presented. To obtain numerical results we introduced approximations for the wavefunctions of core and conduction electrons. Each core (diamagnetic unit) is represented by two, spin-paired, electrons on a simple-Gaussian orbital with characteristic parameter α . For oxygen anions in the cuprates the value of α is found to be 0.20 au^{-2} when scaled to the (gauge) atomic density of Cs metal [48]. The wavefunction of a conduction electron is approximated by a theta function, i.e. a plane wave modulated by simple-Gaussian functions at the sites of the diamagnetic (Wannier) cores, with characteristic parameter β . The unit consisting of two conduction electrons and one core leads to s-wave pairing; anisotropic components of the pairing potential can be introduced formally by considering coupling via nearest-neighbor diamagnetic units. In view of the high (octahedral) symmetry of oxygen anions in the bismuthates, such anisotropy of the pairing potential (and thus of the gap function) is neglected. As mentioned earlier, experiments [12,13] show that pairing in $(Ba, K)BiO_3$ has s-wave symmetry.

The result of the formal analysis is that W is obtained as a function of the parameters α , β , and k_F

$$W = W(\alpha, \beta, k_F), \quad (2)$$

which function can be evaluated for different values of these parameters. We emphasize that W also contains the direct (Coulomb) repulsion between the conduction electrons. Values of W , as a function of β for different k_F and with $\alpha = 0.20 \text{ au}^{-2}$, as well as different α (i.e. different 'size' of the diamagnetic units) at $k_F = 0.341 \text{ au}^{-1}$, are plotted in [48–51]. Taking $\alpha = 0.20 \text{ au}^{-2}$, $k_F = 0.341 \text{ au}^{-1}$, as an example, it is found that $W < 0$ for $0.11 < \beta < 0.23 \text{ au}^{-2}$, i.e. superconductivity is only possible within these limits.

The quantity β , occurring in the conduction-electron theta function, is a 'localization' parameter determining, at given α and $|k|$, the overlap with the core (Wannier) functions. In the absence of oxygen anions, $\beta = 0$ and the theta function is just a plane

wave. This implies that (in a band formalism) β is a continuous function of the core density ρ ; for dimensional reasons it follows that $\beta \propto \rho^{2/3}$. Additional aspects of the present approach are given in the literature quoted.

2.2. Effects of pressure on critical temperatures

In Section 1.5 it was noted that the effect of pressure on critical temperatures of the bismuthates resembles that observed with the cuprates (hole-doped or electron-doped) both in sign and order of magnitude. Since a satisfactory explanation of pressure effects is very unlikely in the framework of electron-phonon coupling, an analysis of $T_C(P)$ on the basis of indirect-exchange pairing is of particular relevance for the bismuthates. We adopt the general outline given in [51, 52], to which we refer for details.

In the present approach, pressure affects directly the values of β and k_F in the coupling W . Explicitly, $\beta^{3/2}$ is proportional to the core density ρ , whereas k_F varies with volume (V) as $V^{-1/3}$ in the effective-mass approximation. To obtain algebraic expressions, it is observed [49, 52, 53] that the $W(\beta)$ curves for different k_F , at constant α , have the same shape, and that the β -values at maximum $|W|$ do not shift with k_F . Consequently, in the range of β relevant for superconductivity, a separation of β and k_F in W holds to a good approximation. We write

$$|W| = \kappa f(\kappa) g(\beta), \quad (3)$$

with $\kappa \equiv bk_F/\alpha^{1/2}$, a reduced Fermi vector (length). The parameter b is a materials constant; α is, as before, the Gaussian parameter for the diamagnetic unit (O^{2-}). The dimensionless parameter κ characterizes the modulation of the conduction-electron wavefunction across a diamagnetic unit. At small κ this variation is minimal; with increasing κ (filling of the conduction band) the modulation becomes stronger, resulting in a *quenching* of all overlap and exchange integrals. The factor k_F in $|W|$ arises from the density-of-states, whereas the function $g(\beta)$ also contains the effective mass of the quasiparticles.

Using $\langle A\omega \rangle = a\kappa^2$ it follows from (1) and (3) that (β constant)

$$\frac{d \ln T_C}{d\kappa} = \frac{2}{\kappa} + \left(\frac{1}{|W|\kappa} \right) \left(1 + \kappa \frac{d \ln f}{d\kappa} \right). \quad (4)$$

The expression for $d \ln T_C / dP$ is obtained using $d \ln T_C / dP = -(V/B) d \ln T_C / dV$, with $B \equiv -V dP / dV$ the bulk modulus of the system, resulting in [49]

$$\frac{d \ln T_C}{dP} = \left(\frac{1}{3B} \right) \left[2 + \frac{1}{|W|} \left(1 + \kappa \frac{d \ln f}{d\kappa} \right) + \frac{1}{|W|} \frac{2\beta}{g} \frac{dg}{d\beta} \right]. \quad (5)$$

For cation doping at constant β (i.e. constant volume) as in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, in $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_8$ [49, 54] and (approximately) in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, the first two

terms inside the brackets cancel at maximum T_C , as is seen from (4), so that (max. T_C , constant β)

$$\frac{d \ln T_C}{dP} = \frac{1}{3B} \frac{2\beta}{W^2} \frac{d|W|}{d\beta}, \quad (6)$$

independent of the form of $f(\kappa)$. To obtain numerical results in the general case, i.e. with arbitrary κ and β , we must specify $f(\kappa)$. The computed W -curves suggest the simple form $f(\kappa) = \exp(-\kappa^2)$, expressing a rapid decrease of $\kappa f(\kappa)$ in (3) at large κ . Eq. (5) then reads

$$\frac{d \ln T_C}{dP} = \left(\frac{1}{3B} \right) \left[2 + \frac{1}{|W|} (1 - 2\kappa^2) + \frac{1}{|W|} \frac{2\beta}{g} \frac{dg}{d\beta} \right]. \quad (7)$$

The last term of Eq. (7) is usually dominant over the range of cation doping [49, 52], so that $d \ln T_C / dP$ (and thus dT_C / dP) are always *positive* for values of β to the left of the maximum in $|W(\beta)|$. This behavior is found to hold with hole-doped superconductors.

Applying the same formalism we can also calculate the development of T_C at *arbitrary* doping level under pressure [52]. To do so, one observes that the parameters κ and β change with pressure as

$$\kappa(P) = \kappa_0 \exp\left(\frac{P}{3B}\right); \quad \beta(P) = \beta_0 \exp\left(\frac{2P}{3B}\right), \quad (8)$$

with κ_0 and β_0 referring to $P = 0$. Thus, from given κ_0 and β_0 the values of $\kappa(P)$ and $\beta(P)$ follow at once. However, a given $T_C(P = 0)$ does not determine κ_0 and $g(\beta_0)$; in addition, the parameter a in $\langle A\omega \rangle = a\kappa^2$ must be known. For cuprate superconductors, when the main dopant is the oxygen content, this problem can be circumvented as described in [52]. With the bismuthate $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, we interpret (see 1.6) the highest experimental T_C value as representing a maximum on the theoretical $T_C(x)$ curve. As in [52], we introduce an auxiliary maximum temperature T_{Cm} which can in principle be reached from the maximum in the $T_C(x)$ curve by additional cation (hole- or electron-) doping at constant volume (constant β); thus $T_{Cm} \geq \max T_C(x)$. Since in the present analysis we consider the maximum critical temperature to be predominantly determined by the variable κ , not by β , we choose $T_{Cm} = 31.6$ K, i.e. only slightly higher than the maximum of $T_C(x)$. At that temperature we have $\kappa_m^2 = |W_m| + \frac{1}{2}$ as follows from (4) with $f(\kappa) = \exp(-\kappa^2)$; the subscript m refers to T_{Cm} . Then, given $\langle A\omega \rangle_m$ (see next section), $|W_m|$ follows from the equation for T_C . In turn, this yields κ_m , and the parameter a from $\langle A\omega \rangle_m = a\kappa_m^2$, as well as the value of $g_m(\beta)$ from $|W_m|$ and κ_m .

At arbitrary T_C (i.e. doping level), we put $g(\beta) = g_m(\beta)$ in first approximation (doping at constant volume). Then, at that value of T_C , $\kappa(P = 0)$ can be determined. Experimentally it is observed that increasing potassium doping x leads to some shrinkage of the lattice, implying that the value of β (at $P = 0$) depends somewhat on

the doping level. In the numerical results to be presented we compare the pressure dependence of T_C with and without taking shrinkage of the lattice into account.

3. Application to (Ba, K) BiO₃

3.1. Comparison with hole-doped cuprates

The formalism pertaining to the phenomenon of indirect-exchange pairing, set forth in Section 2, will now be applied to properties of (Ba, K)BiO₃. We concentrate on the dependence of T_C on potassium doping content and on applied pressure (external or ‘chemical’), a principal reason being that properties close to the transition temperatures are not affected by complications arising from microscopic morphology of the sample, such as grain boundaries, sintered or single-crystal structures, etc.. The characteristic lengths in superconductivity, i.e. magnetic penetration depths and GL coherence lengths, diverge at T_C . A prime example of this lack of sensitivity to micro-structural properties is the transition temperature itself. Conversely, the analysis of properties close to T_C provides a direct test for the validity of proposed pairing mechanisms.

As in the cuprates, Cooper-pair formation in the bismuthates is assumed to be mediated by oxygen anions. This analogy affords a direct extension of earlier analyses [49, 52] to the bismuthates as far as the effect of pressure is concerned. Doping effects, on the other hand, are fundamentally different: in the cuprates, (cation) hole doping (e.g. in La_{2-x}Sr_xCuO₄) leads to the formation of new states (or a transfer of spectral weight) in the charge-transfer gap of the undoped, antiferromagnetic, insulator, with (indirectly) *increasing* conduction-electron density (increasing k_F) at higher doping content [49]. In contrast, potassium doping of diamagnetic BaBiO₃ entails a suppression of the static CDW and finally results in metallic character and superconductivity. Upon further doping, T_C decreases as a result of *decreasing* conduction-electron density (decreasing k_F).

Adopting for (Ba, K)BiO₃ the same formalism as with hole-doped cuprates, the coupling strength $|W|$ is a function of the three parameters α , β , and k_F (or k_F replaced by $\kappa \equiv bk_F/\alpha^{1/2}$), with α referring to oxygen anions in both cases. The expression for T_C is given by (1), in which the pre-exponential factor $\langle A\omega \rangle$, proportional to the Fermi energy, is a characteristic temperature for indirect-exchange pairing. In view of the fact that coupling in (Ba, K)BiO₃ is also mediated by oxygens, we consistently assume that $\langle A\omega \rangle$ in (Ba, K)BiO₃, at maximum T_C , is of order 200 K at ambient pressure, within a range of about 180–220 K as found with the cuprates [47, 48].

It should be noted that an accurate value for the parameter α of (Wannier) oxygen anions in doped (Ba, K)BiO₃ cannot be given because of lack of information regarding charge distributions in this system. If we take, as limits, 3 and 2 anions O²⁻ in

a volume of $78 \text{ \AA}^3$ per molecular unit, then the α values, scaled to the gauge density of Cs metal [48], amount to 0.18 and 0.23 au^{-2} , respectively. We assume an average of 0.20 au^{-2} , as in the cuprates.

Considering the parameter β , a *gauge value* (0.15 au^{-2}) was adopted for the first member (one CuO_2 layer per molecular unit) of the Ti_2 -series [48]. This enabled a calculation of β at arbitrary ('active') oxygen density in all cuprates since β is proportional to $\rho^{2/3}$, with ρ the oxygen density. However, $(\text{Ba}, \text{K})\text{BiO}_3$ cannot be incorporated in the same procedure: β is a measure, at given α and k_F , of the overlap between the Fermi-liquid conduction band and the oxygen valence band, which needs not be similar for the two types of compounds. This implies that, although β is again $\propto \rho^{2/3}$, the proportionality constant will be different in the two cases.

As a substitute for the gauge value in hole-doped cuprates, it appears possible (see below) to *accurately* determine β of $(\text{Ba}, \text{K})\text{BiO}_3$, at ambient pressure, on the basis of the measured value of dT_C/dP , for which we take 0.38 K/GPa determined by Beille et al. [44]. This procedure necessitates knowledge of the bulk modulus $B \equiv -VdP/dV$ of $(\text{Ba}, \text{K})\text{BiO}_3$. Schilling and Klotz [41] adopt for B the same 157 GPa as with BaBiO_3 [55]. From a model calculation Cornelius et al. [56] later deduced 141 GPa for $(\text{Ba}, \text{K})\text{BiO}_3$ and 133 GPa for BaBiO_3 . The only directly measured value, $200 \pm 10 \text{ GPa}$, of B for $(\text{Ba}, \text{K}) \text{BiO}_3$ was recently reported by Akhtar et al. [57]; it is probably considerably too high, considering their result of $215 \pm 10 \text{ GPa}$ with BaBiO_3 . In the numerical calculations we take $B = 150 \text{ GPa}$.

3.2. Numerical results

On the basis of the procedure described in Section 2.2, the following calculations are carried out:

(A) We first determine the relationship between β and $\langle A\omega \rangle$ at maximum $T_C(x) = 31.5 \text{ K}$ under the *constraint* that $dT_C/dP = 0.38 \text{ K/GPa}$ [44]. Computationally it is somewhat simpler to specify that T_C at a pressure of 2 GPa must be 32.20 K , while allowing a margin in T_C of $\pm 0.05 \text{ K}$. As outlined before, a chosen value of $\langle A\omega \rangle_m$ leads directly to $|W_m|$, κ_m , $g_m(\beta)$ as well as to the value of a in $\langle A\omega \rangle_m = a\kappa_m^2$. Conversely, by varying β , we can determine maximum and minimum values of $\langle A\omega \rangle_m$ compatible with the condition $T_C(P = 2 \text{ GPa}) = 32.20 \pm 0.05 \text{ K}$, taking $B = 150 \text{ GPa}$. The results of the analysis are presented in the following Fig. 1. The parameter β is varied between 0.160 and 0.175 au^{-2} , and the scale of $\langle A\omega \rangle$ ranges up to 500 K . The upper curve represents combinations $\{\langle A\omega \rangle, \beta\}$ for which T_C at $P = 2 \text{ GPa}$ is 32.25 K , the lower curve applies for 32.15 K and the middle curve for $T_C = 32.20 \text{ K}$.

It is seen that with $\langle A\omega \rangle_m \approx 200 \text{ K}$, as in the cuprates, the value of β at ambient pressure is very close to 0.172 au^{-2} . The limiting $\langle A\omega \rangle_m$ are here 182 and 236 K , indicating a weak dependence of T_C on $\langle A\omega \rangle_m$ relative to variations in β . The value of

Fig. 1. Relation between the pre-exponential factor $\langle A\omega \rangle$ (degrees K) in Eq. (1), for $T_c = 31.5$ K, and the ambient-pressure conduction-electron parameter β (au^{-2}), under the constraint that T_c at $P = 2$ GPa equals 32.20 ± 0.05 K (see text). For $\langle A\omega \rangle \approx 200$ K (middle curve) the value of β , thus determined, amounts to 0.172 au^{-2} .

$\langle A\omega \rangle_m$ for $T_c(P = 2 \text{ GPa}) = 32.20$ K is 209 K. The calculated $\beta = 0.172 \text{ au}^{-2}$ lies clearly to the left of the value at maximum $|W(\beta)|$, $\beta = 0.184 \text{ au}^{-2}$, i.e. (Ba, K) BiO_3 is a *hole-doped* superconductor in the indirect-exchange approach.

(B) Next, we calculate the dependence of T_c on the parameter κ , i.e. on the Fermi vector k_F , with $T_{cm} = 31.6$ K. Three different values 182, 209, and 236 K are taken for $\langle A\omega \rangle_m$ i.e. those values determined above compatible with $T_c = 32.20 \pm 0.05$ K at $P = 2$ GPa. The curves $T_c(\kappa)$ in the three cases are readily computed from (1), with $\langle A\omega \rangle = a\kappa^2$ for arbitrary κ , and with constant $g(\beta) = g_m(\beta)$, i.e. at constant volume of the system. The resulting $T_c(\kappa)$ curves are presented in Fig. 2 for, from the right, $\langle A\omega \rangle_m = 182, 209$, and 236 K, respectively.

It is seen from the figure that the three curves are almost the same; in fact they are practically coinciding for $\kappa \leq 1$ i.e. in the physical region (values $\kappa > 1$ would occur assuming that $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ remains metallic for $x < 0.35$). The values of κ_m lie close together, amounting to 1.035, 1.015, and 0.999 at $\langle A\omega \rangle_m = 182, 209$, and 236 K, respectively. The weak dependence of T_c on $\langle A\omega \rangle_m$ is demonstrated by these results.

(C) In the next step we determine the relationship between potassium doping content x in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ and κ (i.e. k_F), making use of the $T_c(x)$ data given by Pei et al. [7]. We select $x = 0.35, 0.45, 0.47$ and 0.52 , corresponding with $T_c = 31.5, 25, 23$, and 16 K (the last value extrapolated from the $T_c(x)$ curve). The reason for this choice is that Schirber et al. [43] studied pressure effects on samples with the last three T_c values mentioned, which we consider in more detail below. It was mentioned in the Introduction that the lattice shrinks somewhat under increasing doping, with the pseudo-cubic lattice parameter $a(x)$ varying as $4.3548 - 0.1743x$ [7]. The calculations

Fig. 2. Dependence of the critical temperature of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ on the reduced Fermi vector $\kappa = \hbar k_F / \alpha^{1/2}$. Three values 182, 209, and 236 K were used for the pre-exponential factor $\langle A\omega \rangle$ in Eq. (1), at $T_{\text{cm}} = 31.6$ K (see text). Note that increasing $\kappa(k_F)$ corresponds to lower potassium doping x . The experimental κ values range up to $\kappa \approx 1$; larger values refer to hypothetical metallic $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with $x < 0.35$.

of $\kappa(x)$ are carried out in two versions: *with* and *without* compression induced by doping. In the first case we have, denoting the lattice parameter by $a(x)$, and starting from $x = 0.35$, that $\beta(x) = \beta(0.35) [a(0.35)/a(x)]^2$, since β is proportional to $V^{-2/3} = a^{-2}$. The results for $\kappa(x)$ including shrinkage are compared with those neglecting volume changes, in which case $\beta(x) = \beta(0.35)$, all x . It may be remarked that external pressure simulating shrinkage through doping is quite considerable: 6.3 GPa for compression from $x = 0$ to 0.35, and 2.7 GPa from $x = 0.35$ to 0.5 (bulk modulus 150 GPa). As in (A) and (B), we choose $\langle A\omega \rangle_m = 182, 209$, and 236 K. Then we calculate from (1), including or excluding compression, with each of the four $T_C(x)$ and the three $\langle A\omega \rangle_m$, the corresponding *two* solutions $\kappa(x)$. One of each of set of κ values is smaller than κ_m ('underdoped' with respect to κ_m), whereas the second value is larger than κ_m ('overdoped'). The solution $\kappa < \kappa_m$ applies in the present case, since k_F decreases with increasing x .

The results, marked 'IN' when compression is included, 'EX' when excluded, show a (practically) *linear* dependence $\kappa(x) = cx + d$ with values of c and d as listed in Table 1.

The (linear) relationship between κ and x implies that a simple 'hole count' effect of x and k_F is not applicable [5]. Namely, on the basis of an effective-mass approximation we expect a linear relationship between κ^3 and x , as was found to hold accurately for $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_y$ [54]. In $(\text{Ba}, \text{K})\text{BiO}_3$ part of the hole doping is absorbed by the lattice in terms of a local redistribution of charges, resulting in a minor compression.

(D) In the final state of the analysis we determine the pressure dependence of T_C at different potassium levels x , applying the procedure outlined in 2.3. The results are to be compared with experimental data of Schirber et al. [43] and of Beille et al. [44].

Table 1
Values of the coefficients c and d in the linear dependence
 $\kappa(x) = cx + d$ (see text)

$\langle A\omega \rangle_m$ (K) =	182	209	236
c 'IN'	-2.199	-2.135	-2.078
c 'EX'	-2.157	-2.089	-2.030
d 'IN'	1.780	1.739	1.703
d 'EX'	1.767	1.724	1.687

Fig. 3. Results for dT_c/dP (unit 10^{-2} K/GPa) and $d \ln T_c/dP$ (units 10^{-2} GPa $^{-1}$) as a function of potassium doping level x in $Ba_{1-x}K_xBiO_3$. The curves marked 'IN' ('EX') are calculated taking into account (ignoring) shrinkage of the lattice with increasing x . The value for the parameter β is 0.172 au^{-2} at $P = 0$ and $x = 0.35$; the bulk modulus is 150 GPa.

The calculations are based on the value $\beta = 0.172 \text{ au}^{-2}$ at $x = 0.35$ ($P = 0$) and on $B = 150$ GPa for the bulk modulus. Once again, we choose $\langle A\omega \rangle_m = 182, 209$, and 236 K. With varying x , we use the $\kappa(x)$ and $\beta(x)$ relations (at $P = 0$) obtained in (C), including and excluding compression. The dependence of κ and β on pressure was given in 2.2.

In Fig. 3 the results for dT_c/dP (units 10^{-2} K/GPa) and $d \ln T_c/dP$ (units 10^{-2} GPa $^{-1}$) are given, as a function of x , both for including (IN) and excluding (EX) shrinkage, and with $\langle A\omega \rangle_m = 209$ K. The qualitative behavior is the same in either case: whereas dT_c/dP decreases (after a slight increase when ignoring shrinkage) with increasing x (decreasing T_c), the values of $d \ln T_c/dP$ slowly rise with x .

The results at $\langle A\omega \rangle_m = 182$ or 236 K are very similar, showing a slight upward shift for higher $\langle A\omega \rangle_m$ in dT_c/dP (and thus $d \ln T_c/dP$).

In a last step we evaluate the development of T_c with pressure up to 20 GPa for the system with maximum $T_c = 31.5$ K at $P = 0$. In Fig. 4 these results are given at

Fig. 4. Dependence of the critical temperature on pressure, $T_C(P)$, for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with $T_C = 31.5$ K ($x = 0.35$) at $P = 0$. The three curves are calculated using 182 K (upper), 209 K (middle) and 236 K (lower curve) for the pre-exponential factor $\langle A\omega \rangle$ in Eq. (1), at $T_{Cm} = 31.6$ K (see text). The maximum T_C reached is 34.3, 34.5, and 34.7 K, respectively, at the same pressure of 15 GPa.

$\langle A\omega \rangle_m = 182$, 209, and 236 K, with dT_C/dP (units 10^{-2} K/GPa) at $P = 0$ equal to 34, 37 and 39, respectively. In all three cases, T_C reaches a maximum at $P = 15$ GPa, and at values 34.3, 34.5, and 34.7 K, in the same order. We thus see that, also for $T_C(P)$, a wide range of $\langle A\omega \rangle_m$ leads to results which are strikingly close.

3.3. Comparison with experimental pressure results on $(\text{Ba}, \text{K})\text{BiO}_3$

The numerical results for dT_C/dP at different potassium doping levels x , and of $T_C(P)$ calculated with $T_C(P = 0) = 31.5$ K, reported in 3.2, will now be confronted with experimental data. Compared with cuprate superconductors, this information is scarce, and in part conflicting. As mentioned in 1.5, Beille et al. [44] measured $dT_C/dP = 0.38$ K/GPa on a single crystal at $T_C = 31.5$ K, which value we adopted as a *gauge* for the determination of β ($= 0.172 \text{ au}^{-2}$) at ambient pressure. At pressures beyond 1.4 GPa, these authors observed a strongly nonlinear effect on T_C , which they ascribe to a possible structural transition induced by pressure, or to a shift of the phase diagram. Uwe et al. [58] measured $dT_C/dP = 0.74$ K/GPa, i.e. twice that of [44], on a sample with $T_C = 31$ K at $P = 0$. These authors report superconductivity to occur between $x = 0.25$ and 0.40, whereas Pei et al. [7], from their detailed analysis, determine these limits as 0.35 and 0.50.

They [7] do observe resistive onsets of superconductivity for $0.30 \leq x < 0.35$, but zero resistance is not achieved at any temperature above 10 K. Furthermore, the authors of [58] find anomalous values of the lattice parameter with samples annealed in oxygen.

The only experimental information on dT_C/dP at varying doping x stems from Schirber et al. [43]. They found for samples with unspecified doping levels that

$dT_C/dP = 0.5 \pm 0.2$ at $T_C = 25$ K, 0.8 ± 0.2 at 23 K, and 1.0 ± 0.2 K/GPa at $T_C = 16$ K, i.e. *increasing* with decreasing T_C , using helium (mostly in the solid state) as a pressure medium and a RF impedance method in measuring T_C . (We note that the lowest T_C measured by Pei et al. [7] is 20 K, at $x = 0.50$, the solubility limit of potassium.) The corresponding values for $d\ln T_C/dP$ amount, in units 10^{-2} GPa $^{-1}$, to about 2.0 at $T_C = 25$ K, 3.5 at 23 K, and 6.3 at 16 K, i.e. a *steep* increase going to lower T_C .

Comparing the results of [43] with those of the present analysis, presented in Fig. 3, the correspondence is found to be only slight. Whereas according to [43] dT_C/dP *decreases* for higher T_C , we calculate an *increase* in the same direction. The calculated values of $d\ln T_C/dP$ decrease towards higher T_C , as in [43], but the lowering is much smaller than that reported by Schirber et al.

Regarding a possible reason for these discrepancies, we might mention that the authors of [43] used identically the same technique as that applied earlier [59] in measurements of dT_C/dP in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, finding an increase at higher T_C . Their values for $d\ln T_C/dP$ also show an *increase* towards higher T_C , in contradiction with resistivity measurements by Tanahashi et al. [60], in which a minimum of $d\ln T_C/dP$ was measured near maximum T_C . A detailed comparison is found in the review article by Schilling and Klotz [41]. Our theoretical analysis of this system [49], very similar to the present one, yielded excellent agreement with the experimental results of Tanahashi et al. [60].

Further, lack of information in [43] on the doping levels precludes a comparison with $T_C(x)$ results of Pei et al. [7]. It is clear that more detailed experimental information, at controlled doping x , is called for to enable a reliable comparison to be made between experimental findings and theoretical predictions regarding the effect of pressure on T_C in $(\text{Ba}, \text{K})\text{BiO}_3$.

4. Summary of results and concluding remarks

In the present paper we analyzed superconductivity in the bismuthate $(\text{Ba}, \text{K})\text{BiO}_3$, concentrating on the dependence of the critical temperature on potassium doping content and on the effect of pressure (external or ‘chemical’). From a review of present interpretations of superconductivity, including $\text{Ba}(\text{Pb}, \text{Bi})\text{O}_3$ (Section 1), we concluded that an electron–phonon coupling mechanism, assumed on the basis of the observed oxygen isotope effect and the interpretation of tunneling experiments, leads to severe difficulties when confronted with experimental doping and pressure results (Section 1.6).

We then proceeded (Section 2) to the application of an indirect-exchange coupling mechanism between conduction electrons via closed-shell oxygen anions (oxygen valence band), following analyses presented earlier [47–49, 52, 54] of high- T_C superconductivity in (hole-doped) cuprates. The presumed analogy affords a detailed numerical evaluation of doping and pressure effects on T_C (Section 3). A *gauge* value

for the conduction-electron parameter β was determined from the experimental pressure gradient $dT_C/dP = 0.38 \text{ K/GPa}$ measured by Beille et al. [44] at $T_C = 31.5 \text{ K}$. The results of this calculation are presented in Fig. 1.

The numerical calculations of T_C at varying doping (x) in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ and pressure (P) were carried out in two versions: *with* and *without* incorporating the observed shrinkage of the cubic lattice parameter with increasing potassium content. Results for $dT_C(x)/dP$ and $d\ln T_C(x)/dP$ are presented in Fig. 3; those for $T_C(P)$ at $x = 0.35$ in Fig. 4. The only available experimental information on $dT_C(x)/dP$, by Schirber et al. [43], although agreeing in sign and order of magnitude with the calculated values, deviates in its dependence on T_C . The calculations show that $T_C(P)$, from an initial value of 31.5 K at $P = 0$, reaches a maximum of only $34.5 \pm 0.2 \text{ K}$ (depending on the value of the characteristic temperature $\langle A\omega \rangle$ at maximum T_C in Eq. (1) for T_C), then decreases rapidly at higher pressures. To our knowledge, no experimental results are known in that pressure range. The lack of such experiments, at controlled potassium doping content, precludes a comparison with the detailed numerical results obtained in the present analysis.

An explanation for the semiconductivity of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ in the monoclinic ($x < 0.1$) and orthorhombic ($0.1 < x < 0.35$) phases lies outside the scope of the present analysis. We can, nevertheless, calculate T_C for the (hypothetical) case when there is no breathing-mode distortion in BaBiO_3 , whether such a distortion is driven by Fermi-surface instability [36] or associated with a true minimum in the total (static) lattice energy [33, 35]. To this end, we extend the calculations of T_C for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ to $x = 0$, including and excluding shrinkage of the lattice, while taking again (Section 3) for the characteristic temperature $\langle A\omega \rangle$ in (1) the values 182, 209, and 236 K. The results are: $T_C = 0.09 \text{ K}$, 0.13 K , and 0.17 K at $\langle A\omega \rangle = 182, 209$, and 236 K , respectively, *including* shrinkage, whereas *without* this effect $T_C = 0.26 \text{ K}$ at $\langle A\omega \rangle = 209 \text{ K}$. This shows that even without breathing-mode distortion, and for metallic BaBiO_3 , this system would *not* (or at best hardly) be a superconductor. The reason is mainly a too large value of k_F ; the pressure gradient dT_C/dP is even slightly negative (-0.2 to $-0.3 \times 10^{-2} \text{ K/GPa}$) in undoped BaBiO_3 .

As a consequence of the calculated T_C dependence on doping, the (any) superconductor-to-semiconductor phase transition in $(\text{Ba}, \text{K})\text{BiO}_3$ must occur at a critical doping to the *left* of the theoretical maximum in $T_C(x)$, since the free-energy curves of the two phases can only intersect in that range. This obviously applies as well for $\text{Ba}(\text{Pb}, \text{Bi})\text{O}_3$, both for Pb- and Bi-doping of the respective end member. The electron-doped cuprate $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ remains an (antiferromagnetic) semiconductor up to $x = 0.14$ [62]; its $T_C(x)$ dependence resembles that of $(\text{Ba}, \text{K})\text{BiO}_3$, but with a steeper decrease of T_C at larger doping. We recall that calculations assuming electron-phonon coupling in the bismuthates [29–31, 33] predict a continuous decrease of T_C with increasing K or Pb doping, ignoring phase transitions. It is of interest to note that Chaillout et al. [63, 64], in a neutron powder diffraction experiment, detected two types of BaBiO_3 structures with different samples at room temperature, one of which showed a large difference in the two Bi-O bond lengths, while in the

other phase these lengths were practically equal. No electrical properties were reported on this second phase; the authors interpreted the observation in terms of a different degree of $\text{Bi}^{3+}-\text{Bi}^{5+}$ disorder.

An analysis of superconductivity in $\text{Ba}(\text{Pb},\text{Bi})\text{O}_3$ was not undertaken in the present paper. We expect that this may be possible by analogy with *electron*-doped cuprates and alkali-doped fullerenes [50, 51] in which the corresponding β values lie to the *right* of the maximum in the coupling strength $|W(\beta)|$, leading generally (see Eq. (7)) to negative values of dT_C/dP . This aspect (together with a still somewhat lower density-of-states than in $(\text{Ba},\text{K})\text{BiO}_3$) distinguishes between the two types of bismuthate superconductors in the framework of indirect-exchange Cooper-pair formation.

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Note added in proof

Very recently, Zhao and Morris [65] measured the oxygen isotope coefficient, α_0 , in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ for three different potassium concentrations, establishing a strong x dependence: $\alpha_0 = 0.21 \pm 0.02$ for $x = 0.45$; 0.26 ± 0.02 for $x = 0.375$, and 0.34 ± 0.02 for $x = 0.36$. The authors combine their experiments with measurements of the temperature dependence of the Meissner fraction of the susceptibility, related to that of the magnetic penetration depth. For an s-wave superconductor and temperatures $T < 0.5T_C$ this leads to values of the reduced gap for the three compositions x , resulting in $2\Delta(0)/k_B T_C = 4.0 \pm 0.2$, 4.5 ± 0.2 , and 4.8 ± 0.2 for $x = 0.45$, 0.375 and 0.36 , respectively. In a further step, the authors connect $2\Delta(0)/k_B T_C$ to the quantity $k_B T_C/\hbar\omega_{\text{in}}$ of the Allen–Dynes equation, using a semi-empirical relation given by Carbotte [66]. Assuming $\mu^* = 0.10$ for the Coulomb pseudopotential, the three values of $k_B T_C/\hbar\omega_{\text{in}}$, thus estimated, lead to those for the electron-phonon coupling parameter λ in the Allen–Dynes equation, from which a (α_0, λ) plot is constructed. Isotope coefficients as a function of λ are then calculated on the basis of the Allen–Dynes equation. It appears that agreement with the (α_0, λ) dependence is obtained only by assuming that the electron-phonon coupling λ depends on the oxygen mass, with $d\ln\lambda/d\ln M_0 = 0.2$. Such a dependence, the authors argue, may be due to anharmonicity of the oxygen phonon modes and/or to a breakdown of the Migdal adiabatic approximation.

It is difficult to assess the possible reliability of such an extremely intricate procedure. We note that the equations used, in particular the relation between the reduced gap and the parameter $k_B T_C/\hbar\omega_{\text{in}}$, is valid for low- T_C superconductors only, where

$k_B T_C / \hbar \omega_{\text{in}} < 0.25$. Affronte et al. [67] recently showed, from measurements of the upper critical field of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, that standard expressions [66] lead to $k_B T_C / \hbar \omega_{\text{in}} > 0.4$, to which no value of the electron-phonon coupling parameter λ in the Allen–Dynes equation corresponds. The latter authors conclude that $(\text{Ba}, \text{K})\text{BiO}_3$ cannot be treated as a conventional weakly-coupled superconductor, although the reduced gap $2\Delta(0)/k_B T_C$ is not excessively large.

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