Physica C 170 (1990) 405–410
North-Holland

Thermodynamic analysis of $Ba_xK_{1-x}BiO_3$ using the Eliashberg theory

O. Navarro [1] and R. Escudero

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, 04510 Mexico D.F., Mexico

Received 22 May 1990
Revised manuscript received 6 August 1990

In order to understand the mechanism that gives rise to superconductivity in the ceramic superconductors of the type $Ba_xK_{1-x}BiO_3$, we analyze the thermodynamic properties with the use of the Eliashberg equations. For these calculations we used the electron–phonon spectral density function $\alpha^2(\omega)F(\omega)$, calculated by Shirai et al. [1] from first principles for two different K concentrations, $x=0.5$ and $x=0.7$.

1. Introduction

The recent discovery of superconductivity near 30 K in $Bi_xK_{1-x}BiO_3$ (BKBO) [2,3] provides a new opportunity to examine the pairing mechanism in perovskite superconductors. The compound BKBO has engendered much interest because it is the first oxide superconductor without Cu that has a transition temperature, T_c, above that of the best intermetallic superconductor. Another feature of this system is that the structure is three-dimensional [3,4], with the important Bi–O bonds forming a cubic network, which excludes any analog of the two-dimensional Cu–O planes believed to be responsible for superconductivity in the copper-oxide-based superconductors.

Measurements of the oxygen isotope content in BKBO have led to conflicting results, indicating either a phonon [5] or a non-phonon [6] mediated pairing mechanism. In this high-T_c oxide a magnetic interaction is not expected to be the cause of superconductivity [6]. Therefore, it is important to make an investigation of the superconductivity in BKBO on the basis of the conventional electron–phonon pairing.

In order to test if phonons could be responsible for the high transition temperature in BKBO, we make an analysis of the thermodynamic properties using the Eliashberg theory of superconductivity [7] and the Eliashberg function, $\alpha^2(\omega)F(\omega)$, obtained by Shirai et al. [1] calculated from first principles, in which they are assuming that $F(\omega)$ represents only the phonon density of states of the crystalline structure.

In fig. 1 we present three different Eliashberg functions, $\alpha^2(\omega)F(\omega)$, for BKBO, with different K concentrations. Notice how the spectral weight at 42 meV and at 62 meV is changing for the different K concentrations. In other words this means that the main peak of the different $\alpha^2(\omega)F(\omega)$ curves is localized each time closer to the maximum of the functional derivative [8–11] of T_c with respect to $\alpha^2(\omega)F(\omega)$, $\delta T_c/\delta(\alpha^2(\omega)F(\omega))$, which should result in the optimum critical temperature, as we will see later. According to the criterion given by the functional derivative of T_c, we deduce that the maximum transition temperature is still a little far away from the optimum for this compound. Experimentally, this problem may be related to the chemical difficulties found when introducing the correct amount of potassium into the structure, or due to the structural instability found at the maximum T_c by Pei et al.

---

[1] On leave from Escuela de Ciencias Físico Matemáticas de la Universidad Autónoma de Sinaloa.

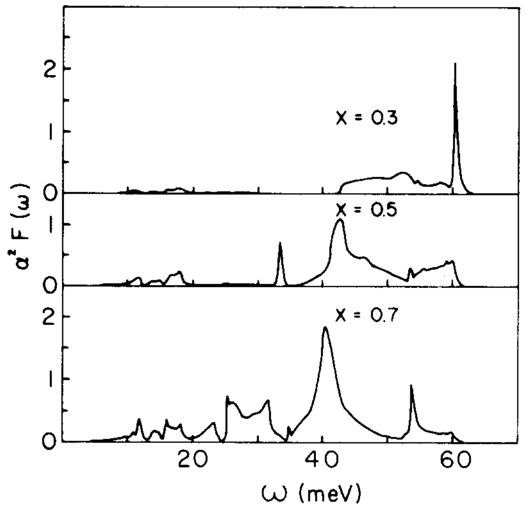

Fig. 1. The electron–phonon spectral density $\alpha^2(\omega)F(\omega)$ for $Ba_xK_{1-x}BiO_3$ calculated by Shirai et al. [1] for three different K concentrations.

[12] in their structural phase characterization of BKBO.

The functional derivative $\delta T_c/\delta(\alpha^2(\omega)F(\omega))$ has the following physical meaning. If $\alpha^2(\omega)F(\omega)$ is changed by a small amount $\Delta(\alpha^2(\omega)F(\omega))$, the resulting change of the transition temperature is given by

$$\Delta T_c = \int_0^\infty d\omega \frac{\delta T_c}{\delta(\alpha^2(\omega)F(\omega))} \Delta(\alpha^2(\omega)F(\omega)). \quad (1)$$

The functional derivative of T_c with respect to $\alpha^2(\omega)F(\omega)$ has been calculated by Bergmann and Rainer [8] for several superconductors. Their main conclusions are: the functional derivative is insensitive to the difference in shapes of the corresponding $\alpha^2(\omega)F(\omega)$ spectra, it starts linearly at the origin, has a maximum slightly above $\omega = 2\pi T_c$, and then decreases monotonically. Bergmann and Rainer [8] have also given an analytic proof that $\delta T_c/\delta(\alpha^2(\omega)F(\omega))$ is always positive and is linear in ω at small frequencies.

In section 2 we give some necessary theoretical details. In section 3 we present our numerical results and discussion, and in section 4 we provide a short conclusion.

2. Theoretical background

The superconducting properties of a material with phonon-mediated pairing can be calculated at any finite temperature T from its spectral function $\alpha^2(\omega)F(\omega)$ and Coulomb potential parameter μ^* by solving the Eliashberg equations. These equations which are conveniently written on the imaginary frequency axis and so involve the Matsubara frequencies $i\omega_n \equiv i(2n+1)\pi T$, $n = 0, \pm 1, \pm 2, \ldots$, have the form [13,14]

$$\bar{\Delta}(i\omega_n) = \pi T \sum_m (\lambda(m-n) - \mu^*) \times \frac{\bar{\Delta}(i\omega_m)}{[\bar{\Delta}^2(i\omega_m) + \bar{\omega}^2(i\omega_m)]^{1/2}} \quad (2)$$

and

$$\bar{\omega}(i\omega_n) = \omega_m + \pi T \sum_m \lambda(m-n) \times \frac{\bar{\omega}(i\omega_m)}{[\bar{\Delta}^2(i\omega_m) + \bar{\omega}^2(i\omega_m)]^{1/2}}. \quad (3)$$

Here

$$\lambda(m-n) = 2 \int_0^\infty \frac{\omega \alpha^2(\omega)F(\omega)\, d\omega}{\omega^2 + (\omega_n - \omega_m)^2}. \quad (4)$$

For $n = m$, $\lambda(m-n)$ is equal to the electron–phonon mass enhancement parameter

$$\lambda = 2 \int_0^\infty \frac{\alpha^2(\omega)F(\omega)\, d\omega}{\omega}. \quad (5)$$

In eqs. (2) and (3), $\bar{\Delta}(i\omega_n)$ is the Matsubara pairing energy function and $\bar{\omega}(i\omega_n)$ is the renormalized frequency.

In addition to a knowledge of the solutions of the Eliashberg equations, we require an expression for the free-energy density difference between the normal and superconducting states, ΔF. This is given by the formula [9,15]

$$\Delta F=2\pi N(0)T\sum_{n>0}\Bigg[2\bigg\{[\bar{\Delta}^2(\mathrm{i}\omega_n)+\bar{\omega}^2(\mathrm{i}\omega_n)]^{1/2}-\bar{\omega}(\mathrm{i}\omega_n)-\frac{\bar{\Delta}^2(\mathrm{i}\omega_n)}{2[\bar{\Delta}^2(\mathrm{i}\omega_n)+\bar{\omega}^2(\mathrm{i}\omega_n)]^{1/2}}\bigg\}-[\bar{\omega}(\mathrm{i}\omega_n)-\bar{\omega}^0(\mathrm{i}\omega_n)]\times\left(\frac{\bar{\omega}(\mathrm{i}\omega_n)}{[\bar{\Delta}^2(\mathrm{i}\omega_n)+\bar{\omega}^2(\mathrm{i}\omega_n)]^{1/2}}-1\right)\Bigg]. \tag{6}$$

Here $N(0)$ is the single-spin electronic density of states at the Fermi surface. The $\bar{\omega}^0(\mathrm{i}\omega_n)$ in eq. (6) is the normal-state value of the renormalized frequency. Also $\gamma(0)$ is the Sommerfeld constant, which is given by

$$\gamma(0)=\tfrac{2}{3}\pi^2k_{\mathrm{B}}^2N(0)(1+\lambda), \tag{7}$$

where k_{B} is the Boltzmann constant.

The critical magnetic field $H_{\mathrm{c}}(T)$ is given by

$$H_{\mathrm{c}}^2(T)/8\pi=|\Delta F|. \tag{8}$$

The deviation function, $D(t)$, is given by

$$D(t)=H_{\mathrm{c}}(T)/H_{\mathrm{c}}(0)-(1-t^2), \tag{9}$$

where $t=T/T_{\mathrm{c}}$. The specific heat jump follows from the second derivative of the free energy according to

$$\Delta C=-T\partial^2\Delta F/\partial T^2. \tag{10}$$

The low temperature energy gap at the gap edge can be obtained by analytically continuing the imaginary axis solution $[\Delta(\mathrm{i}\omega_1),\Delta(\mathrm{i}\omega_2),...]$ to real frequencies and then solving the equation

$$\Delta_0(T)=\mathrm{Re}\,\Delta[T,\omega=\Delta_0(T)]. \tag{11}$$

The N-point Padé approximant method proposed by Vidberg and Serene [16] for $T\ll T_{\mathrm{c}}$ is used for the numerical analytic continuation. In this way one can calculate the zero temperature energy gap, Δ_0.

3. Numerical results and discussion

For calculation of the thermodynamic properties of the oxide superconductor BKBO, we have used two different $\alpha^2(\omega)F(\omega)$ spectra (fig. 1), for concentrations of $x=0.5$ and $x=0.7$ ($T_{\mathrm{c}}=30$ K). These spectra were obtained by Shirai et al. [1] using a tight binding fit to the electronic band structure. We have fitted μ^* ($\omega_{\mathrm{c}}=375$ meV) with the maximum experimental critical temperature for $x=0.7$ ($T_{\mathrm{c}}=30$ K, Cava et al. [3]) and for $x=0.5$ with the critical temperature $T_{\mathrm{c}}=15.6$ K obtained by Hinks et al. [4]. In table I and table II we list several thermodynamic properties calculated from the two $\alpha^2(\omega)F(\omega)$ spectra of BKBO and from an $\alpha^2(\omega)F(\omega)$ of A15 Nb–Ge (strong-coupled superconductor, $T_{\mathrm{c}}=20.09$ K). Our results for Nb–Ge are the same as those calculated by Mitrović et al. [17] for the same sample, and we include them only for comparison.

The thermodynamic results presented in table I and table II are based on numerical solutions of eqs. (2) and (3), with the solutions used to evaluate the free energy difference ΔF. To calculate ΔF it is necessary to know $N(0)$, the single-spin density of electronic states at the Fermi surface. For this calculation we fitted $N(0)$ to the measured [18] $\gamma=1.5$ mJ/(mol K^2) using eq. (7). We obtain $N(0)=0.14$ states/eV for $x=0.7$ and $N(0)=0.21$ states/eV for $x=0.5$ in reasonable agreement with the values obtained using a band-structure calculation [19]. It is worth mentioning that recent specific heat measurements reveal a value for the Sommerfeld constant $\gamma=0.3$ mJ/(mol K^2) [20]. Using this γ value and the $N(0)=0.23$ states/(eV spin cell) given by Mattheiss et al. [19] to estimate λ, we obtain $\lambda=-0.7$, which is an unphysical value. Thus we used the earlier $\gamma=1.5$ mJ/(mol K^2) in our calculations. However, more experimental work seems to be necessary to prove the correct value for γ.

The specific heat difference between the normal and superconducting states, ΔC, can be calculated from eq. (10). For $x=0.7$ the value for $\Delta C/T_{\mathrm{c}}$ is 2.82 mJ/(mol·K^2) in good agreement with experimental data by Batlogg et al. [6], $\Delta C/T_{\mathrm{c}}=2.2$ mJ/(mol·K^2).

We calculated the reduced isotope effect ($T_{\mathrm{c}}\propto M^{-\alpha}$) for $x=0.7$ ($\mu^*=0.12, \lambda=1.18$) using the Garland relation [21],

$$\alpha=\tfrac{1}{2}\{1-[\mu^*/(\lambda^*-\mu^*)]^2\}. \tag{12}$$

Here $\lambda^*=\lambda/(1+\lambda)$. Our result is $\alpha=0.45$, close to the so-called BCS value ($\alpha=0.5$ for a single component system) [22]. Our results are also close to the experimental isotope effect determined by Hinks et al. [5] ($\alpha=0.41\mp0.03$), but disagree with the ex-

Table I
Summary of the parameters calculated with the two $\alpha^2(\omega)F(\omega)$ spectra of BKBO and comparison with calculated values for A15 Nb–Ge (T_c=20.09 K).

	A (meV)	λ	T_c (K)	μ^* (ω_c)	Δ_0 (meV)	ω_c (meV)	Ω_{max} (meV)	γ (mJ/mol K^2)	$N(0)$ [states/ eV spin atom]	$H_c(0)$ (Gauss)	min $D(t)$	max $D(t)$
BKBO												
x=0.5	10.31	0.54	15.56	0.019	2.47	375	62.5	1.5	0.21	0.6930×10^3	−0.0232	–
x=0.7	18.19	1.18	29.94	0.12	5.35	375	62.5	1.5	0.14	0.1415×10^4	–	0.0069
Nb–Ge	8.98	1.47	20.09	0.037	4.01	97.5	32.5	30.3	2.60	0.9457×10^4	–	0.0177

perimental value given by Batlogg et al. [6] (α=0.21). This is an important question that experimentally is convenient to test.

Our calculated values of the electron–phonon coupling parameter λ, using eq. (5) and the $\alpha^2(\omega)F(\omega)$ for several K concentrations, are: λ=0.24 (x=0.3), λ=0.54 (x=0.5) and λ=1.18 (x=0.7). These values are the same as those already calculated by Shirai et al. [1]. The values of λ mentioned before indicate that as the K concentration decreases, the coupling strength increases somewhat faster.

To study the relative influence on the transition temperature of different frequency parts of $\alpha^2(\omega)F(\omega)$, we calculate the functional derivative, $\delta T_c/\delta(\alpha^2(\omega)F(\omega))$, for the two BKBO Eliashberg functions mentioned previously. This functional derivative also shows a maximum at approximately $\omega = 8k_BT_c$. This means that the frequencies which are more important for enhancing T_c are precisely those in the maximum of the curve. From fig. 2 we observe that the curve has a sharper maximum for the sample with the lowest T_c. This maximum becomes broader as T_c increases. In general, the maximum is sharp for weak coupling and gets broader as the coupling increases. The same is shown by the Nb–Ge strong coupling system, studied in detail by Baquero et al. [23], which we have used for comparison with our results. We can also see from fig. 2 that coupling strength (size of λ) increases as the height of the functional derivative curve decreases.

In fig. 3 we plot the calculated critical-field deviation function, $D(t)$, as a function of $t^2=(T/T_c)^2$, for the two BKBO concentrations and Nb–Ge. According to the empirical rule that relates the shape of $D(t)$ to the electron–phonon coupling parameter λ, for $\lambda<1$ $D(t)$ is negative, for $\lambda>1$ $D(t)$ is positive, and for $\lambda\cong1$ $D(t)$ has an S shape. We see that for x=0.7 the coupling is strong and for x=0.5 the coupling is weak (BCS behavior).

Our calculated value for the energy gap, Δ_0 is 5.3 meV (x=0.7), very close to the values of 4.5 to 5.0 meV obtained by optical measurements [24] and in reasonable agreement with tunneling spectroscopy measurements [25] which give Δ_0=6.5 meV. The values of the ratios $2\Delta_0/k_BT_c$, $\gamma(T_c/H_c(0))^2$ and $\Delta C/\gamma T_c$, where $H_c(0)$ is the thermodynamic critical field at temperature T=0 K and ΔC the jump in specific heat at T_c, for x=0.7, give indications of the strong coupling limit.

Table II
Comparison of some parameters calculated for BKBO with the values calculated for Nb–Ge and the values given by the BCS theory.

	$\frac{2\Delta_0}{K_B T_c}$	$-\frac{T_c}{H_c(0)}\left[\frac{dH_c(T)}{dT}\right]_{T_c}$	$\gamma\left[\frac{T_c^2}{H_c(0)}\right]$	$\frac{\Delta C}{\gamma T_c}$
BKBO				
$x=0.5$	3.68	1.71	0.158	1.45
$x=0.7$	4.15	1.83	0.141	1.85
Nb–Ge	4.63	2.08	0.132	2.57
BCS	3.53	1.74	0.168	1.43

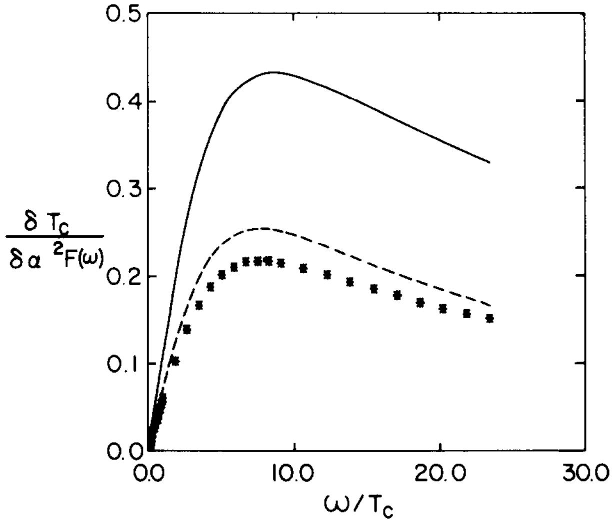

Fig. 2. Calculated values for the functional derivative of T_c with respect to $\alpha^2(\omega)F(\omega)$, $\delta T_c/\delta(\alpha^2(\omega)F(\omega))$, for $Ba_xK_{1-x}BiO_3$ with $x=0.5$ (—) and $x=0.7$ (---), compared to Nb–Ge (***).

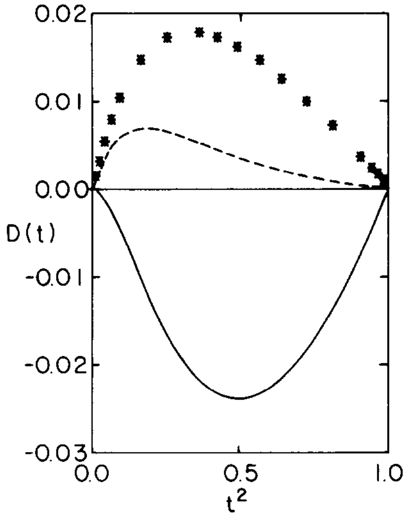

Fig. 3. Calculated values of $D(t)$ for $Ba_xK_{1-x}BiO_3$, with $x=0.5$ (—) and $x=0.7$ (---). For comparison we also show the results for Nb–Ge (***).

Leavens and Carbotte [26] have shown that for many strong coupling superconductors ($1.2<\lambda>2.4$, and $0.10<\mu^*<0.15$) there is a simple relation between T_c and A, where

$$A=\int_0^\infty \alpha^2(\omega)F(\omega)\,d\omega,$$

namely:

$$k_B T_c \simeq 0.1477A. \qquad (13)$$

Using this relation to calculate T_c from the value of A for the $\alpha^2(\omega)F(\omega)$ with $x=0.7$ (note that μ^* falls in the right interval for the applicability of formula (13) and λ falls just below the appropriate range), we obtain $T_c=31$ K, in good agreement with the experimental value of 30 K.

4. Conclusions

The relevant results for this paper can be summarized in the following two points:

1) Based on our calculation of the maximum of the functional derivative of T_c, the optimal critical temperature for this compound can be increased. The experimental restriction is probably due to the difficulty of introducing the correct amount of K into

the crystal structure, or may be due to a structural instability.

2) We have shown that the ceramic superconductor $Ba_xK_{1-x}BiO_3$ can be analyzed as a normal strong-coupled superconductor, in which the Cooper pairing is phonon-mediated, since the $\alpha^2(\omega)F(\omega)$ that we have used contain only the electron–phonon interaction. However, to make a definite judgement of the pairing mechanism in this compound, it would be necessary to make calculations of the quantities given in the tables I and II on the basis of other pairing mechanisms.

Acknowledgements

We would like to acknowledge very useful discussions with Prof. J. Carbotte from McMaster University, Canada. This work was supported by the Programa Universitario de Superconductores, Cerámicos de Alta Temperatura, UNAM, by a grant from Petroleos Mexicanos, PEMEX, and also by the Consejo Nacional de Ciencia y Tecnologia, CONACYT.

References

[1] M. Shirai, N. Suzuki and K. Motizuki, J. Phys.: Condensed Matter 2 (1990) 3553.
[2] L.F. Mattheiss, E.M. Gyorgy and D.W. Johnson, Phys. Rev. B 37 (1988) 3745.
[3] R.J. Cava, B. Batlogg, J.J. Krajewski, R. Farrow, L.W. Rupp Jr., A.E. White, K. Short, W.F. Peck and T. Kometani, Nature 332 (1988) 814.
[4] D.G. Hinks, B. Dabrowski, J.D. Jorgensen, A.W. Mitchell, D.R. Richards, S. Pei and D. Shi, Nature 333 (1988) 836.
[5] D.G. Hinks, D.R. Richards, B. Dabrowsky, D.T. Marx and A.W. Mitchell, Nature 335 (1988) 419.
[6] B. Batlogg, R.J. Cava, L.W. Rupp Jr., A.M. Mujsce, J.J. Krajewski, J.P. Remeika, W.F. Peck Jr., A.S. Cooper and J.P. Espinoza, Phys. Rev. Lett. 61 (1988) 1670.
[7] G.M. Eliashberg, J. Exp. Theoret. Phys. (USSR) (1960) 966, translated in: Sov. Phys.-JETP 11 (1960) 696.
[8] G. Bergmann and D. Rainer, Z. Phys. 263 (1973) 59.
[9] D. Rainer and G. Bergmann, J. Low Temp. Phys. 14 (1974) 501.
[10] B. Mitrović and J.P. Carbotte, Solid State Commun. 37 (1981) 1009.
[11] O. Navarro, MSc. thesis, Univ. Autónoma de Puebla (1986), unpublished.
[12] Shiyou Pei, J.D. Jorgensen, B. Dabrowski, D.G. Hinks, D.R. Richards, A.W. Mitchell, J.M. Newsam, S.K. Sinha, D. Vaknin and A.J. Jacobson, Phys. Rev. B 41 (1990) 4126.
[13] J.M. Daams and J.P. Carbotte, J. Low Temp. Phys. 43 (1981) 263.
[14] P.B. Allen and B. Mitrović, in: Theory of Superconducting T_c, Solid State Physics, Vol. 37, eds. H. Ehrenreich, F. Seitz and D. Turnbull (Academic, New York, 1982) p. 1.
[15] Y. Wada, Phys. Rev. A 135 (1964) 1481.
[16] H.J. Vidberg and J.W. Serene, J. Low Temp. Phys. 29 (1977) 179.
[17] B. Mitrović, E. Schachinger and J.P. Carbotte, Phys. Rev. B 29 (1984) 6187.
[18] J.E. Graebner, L.F. Schneemeyer and J.K. Thomas, Phys. Rev. B 39 (1989) 9682.
[19] L.F. Mattheiss and D.R. Hamann, Phys. Rev. Lett. 60 (1988) 2681.
[20] S.E. Stupp, M.E. Reeves, D.M. Ginsberg, D.G. Hinks, B. Dabrowski and G. Vandervoort, Phys. Rev. B 40 (1989) 10878.
[21] J.W. Garland Jr., Phys. Rev. Lett. 11 (1963) 114.
[22] J. Bardeen, L.N. Cooper and J.R. Schrieffer, Phys. Rev. 108 (1957) 1175.
[23] R. Baquero, J. Gutiérrez-Ibarra, L. Meza, O. Navarro and K.E. Kihlstromn, Rev. Mex. Fis. 35 (1989) 461.
[24] Z. Schlesinger, R.T. Collins and J.A. Calise, Phys. Rev. B 40 (1989) 6862.
[25] J.F. Zasadzinski, N. Tralshawala, D.G. Hinks, B. Dabrowski, A.W. Mitchell and D.R. Richards, Physica C 158 (1989) 519.
[26] C.R. Leavens and J.P. Carbotte, J. Low Temp. Phys. 14 (1974) 195.