The electron–phonon mechanism for resistivity in the high-temperature superconductor system $Ba_{1-x}K_xBiO_3$

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We investigate the temperature-dependent resistivity $\rho(T)$ of single crystals of the high-temperature superconducting compound $Ba_{0.6}K_{0.4}BiO_3$ with a critical temperature $T_c = 30$ K, over the temperature range 4.2–300 K. The experimental data are well approximated by a function $\rho_f(T)$ of Bloch–Grüneisen type, which we obtain within the classical model of the electron–phonon interaction by assuming that the phonon spectrum consists of an acoustic branch with a Debye dispersion law and a narrow optical-phonon peak located a large distance away.

1. INTRODUCTION

Ever since the phenomenon of high-temperature superconductivity was discovered by Bednorz and Müller in 1986,[1] a great number of scientists have spared no effort in pursuing a multifaceted investigation of this new class of compounds—the high-temperature superconductors. Despite the enormous number of papers published, however, the mechanism for high-temperature superconductivity remains unclear to this day, and continues to provoke discussion among supporters of various models, involving, e.g., pure phonons,[2] excitons,[2,3] bipolarons,[4] resonance valence bonds (RVB),[5] and other mechanisms. For this reason, there continues to be a pressing need for investigations of those physical properties of high-temperature superconducting compounds that yield information about the electronic structure of these materials, their phonon spectrum, etc. In particular, the temperature dependence of the electrical resistivity $\rho(T)$, which in traditional superconductors is determined by the very same electron–phonon interaction as the superconducting state, is of particular interest. It is not surprising that the purely linear dependence of $\rho(T)$ on temperature observed in many high-temperature superconductors (e.g., the yttrium, bismuth, and thallium systems) has been widely discussed, and continues to be discussed in the literature; indeed, a good explanation for the behavior of this function is widely regarded as the key to understanding the reasons for the high superconducting transition critical temperatures in this new class of complex metal-oxides.

Our choice of the system $Ba_{1-x}K_xBiO_3$ was determined by the fact that this compound, which is representative of the class of high-temperature superconductors, at the same time possesses a relatively low critical temperature (30 K) and critical fields, which makes it possible, e.g., to measure the function $H_{c2}(T)$ over a wide range of temperatures. Furthermore, $Ba_{1-x}K_xBiO_3$ has a cubic lattice and does not contain Cu or any other magnetic ions, so that the features of its high-temperature superconductivity cannot be explained by the layered nature of the structure or the magnetic properties of the system.

In this paper we present the results of experimental studies of the temperature-dependent electrical resistivity of single-crystal samples of $Ba_{0.6}K_{0.4}BiO_3$ over the temperature interval 4.2–330 K, along with an interpretation of our data within the framework of the classical model of the electron–phonon interaction, using a phonon spectrum consisting of an acoustic branch with a Debye dispersion law, and a narrow optical-phonon peak located far away from the acoustic branch. By analyzing the function $\rho(T)$, we determine the Debye (Θ_D) and Einstein (Θ_E) temperatures of the model spectrum for the acoustic and optical phonons respectively; the values of these quantities coincide with the results of neutron studies of the phonon spectrum of $Ba_{1-x}K_xBiO_3$.[6,7] We then determine the ratio of the electron–phonon interaction constants for acoustic and optical phonons $\lambda_{op}/\lambda_{ac}$. We use the Allen–Dynes intermediate-coupling formula for T_c to obtain absolute values for the electron–phonon interaction constants λ_{op} and λ_{ac} under the assumption that the mechanism for superconductivity in $Ba_{1-x}K_xBiO_3$ is purely due to the electron–phonon interaction.

2. METHODOLOGY AND EXPERIMENTAL RESULTS

The experiments were carried out on single-crystal samples of $Ba_{0.6}K_{0.4}BiO_3$ with characteristic dimensions $2 \times 2 \times 2$ mm³, grown using the method described in Ref. 8. X-ray structural analysis revealed that the samples were single-phase and single-crystal. The critical transition temperature to the superconducting state for these samples was $T_c = 30$ K, and the width of the transition based on levels $0.1 R_0$ to $0.9 R_0$ was, $\Delta T_c = 3$ K. The resistivity was measured using a four-contact scheme for an AC current of 1 mA at a frequency 370 Hz over the temperature range 4.2–330 K.

The functions $\rho(T)$ measured from several samples were identical. In Fig. 1 we show the function $\rho(T)$ for
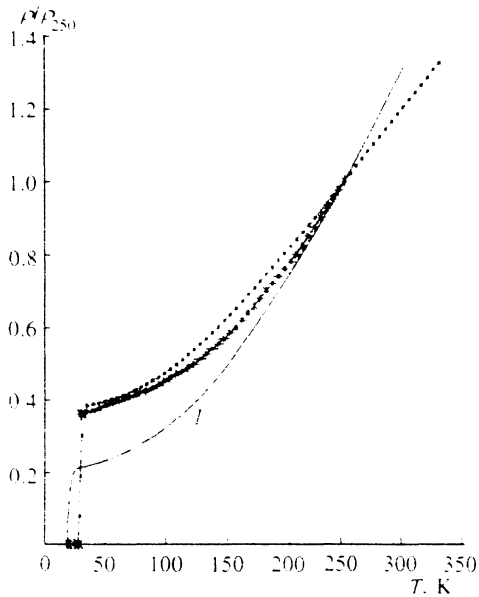
FIG. 1. Temperature dependence of the normalized resistivity in single crystals of $Ba_{0.6}K_{0.4}BiO_3$ (■—our data, *—data of Ref. 9) and resistivity of $Nd_{1.85}Ce_{0.15}CuO_4$ in the ab plane given in Ref. 10 (—).

FIG. 2. The function $d\rho/dT$ in single crystals of $Ba_{0.6}K_{0.4}BiO_3$.

one of these samples along with the published data of Refs. 9,10.

3. DISCUSSION

The temperature dependence of the electrical resistivity of high-quality samples of $Ba_{0.6}K_{0.4}BiO_3$ had a pronounced metallic character, i.e., ρ increases monotonically with temperature, in contrast to that of ceramic samples.[11,12] In single crystals of $Ba_{0.6}K_{0.4}BiO_3$, the function $\rho(T)$ qualitatively coincides with the temperature dependence of the resistivity of single crystals of the layered high-temperature superconductor $Nd_{1.85}Ce_{0.15}CuO_4$ along the ab plane (Fig. 1). At low temperatures, $T < 180$ K, the function $\rho(T)$ is quadratic with temperature, while for $T > 200$ K $\rho(T)$ increases linearly with temperature. This is easily seen in Figs. 2, 3, where the temperature dependences of the derivative $d\rho/dT$ is shown along with ρ plotted as a function of T^2. At first glance, the presence of a broad temperature range (30–180 K) over which a quadratic dependence of $\rho(T)$ is observed in $Ba_{0.6}K_{0.4}BiO_3$ suggests that the mechanism for the electrical resistivity is electron–electron scattering, as was proposed in Ref. 10 to explain the analogous temperature dependence $\rho(T)$ along the ab plane in $Nd_{1.85}Ce_{0.15}CuO_4$. However, if we postulate a dominant role for electron–electron interactions in the scattering of electrons when $T < 180$ K, it is difficult to explain the linear increase in the resistivity with temperature in the range $T > 200$ K. The explanation given in Ref. 10 for the change in character of the function $\rho(T)$ in $Nd_{1.85}Ce_{0.15}CuO_4$ from quadratic at low temperatures ($T < 150$ K) to linear at high temperatures ($T > 180$ K) can hardly be applicable to $Ba_{1-x}K_xBiO_3$. According to Ref. 10, the changeover from $\rho(T) \propto T^2$ to linear behavior at
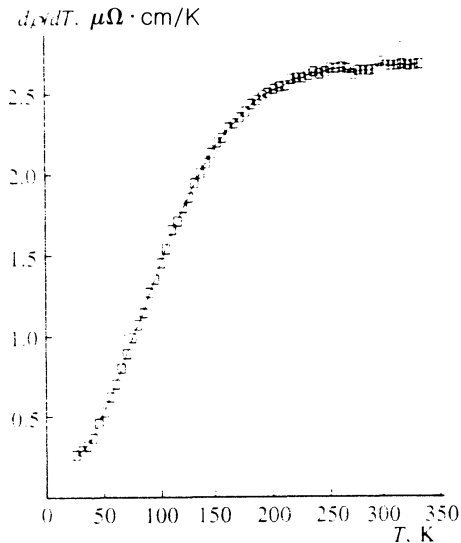
high temperatures is connected with lowered dimensionality of the electronic system in $Nd_{1.85}Ce_{0.15}CuO_4$, which as the temperature increases goes from three-dimensional to two-dimensional. The compound $Ba_{1-x}K_xBiO_3$ possesses a cubic lattice and therefore its electronic system is unlikely to change dimensionality.

For this reason, we have attempted to explain the observed temperature dependence of the resistivity (Fig. 1) within the framework of the usual model of electron–phonon interaction.

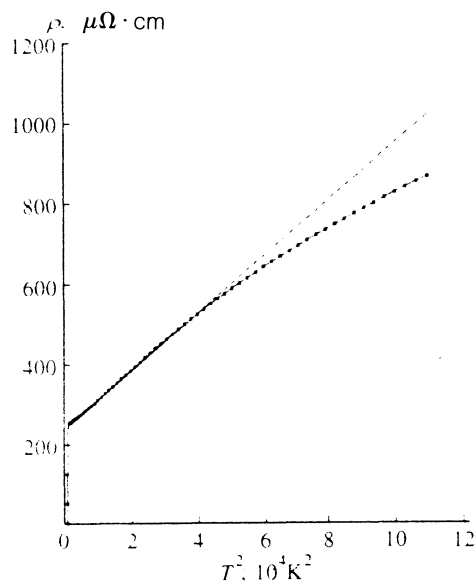The results of neutron-scattering studies and lattice-dynamics calculations[6,7] show that the phonon spectrum in

FIG. 3. The dependence of the resistivity on T^2 in single crystals of $Ba_{0.6}K_{0.4}BiO_3$.

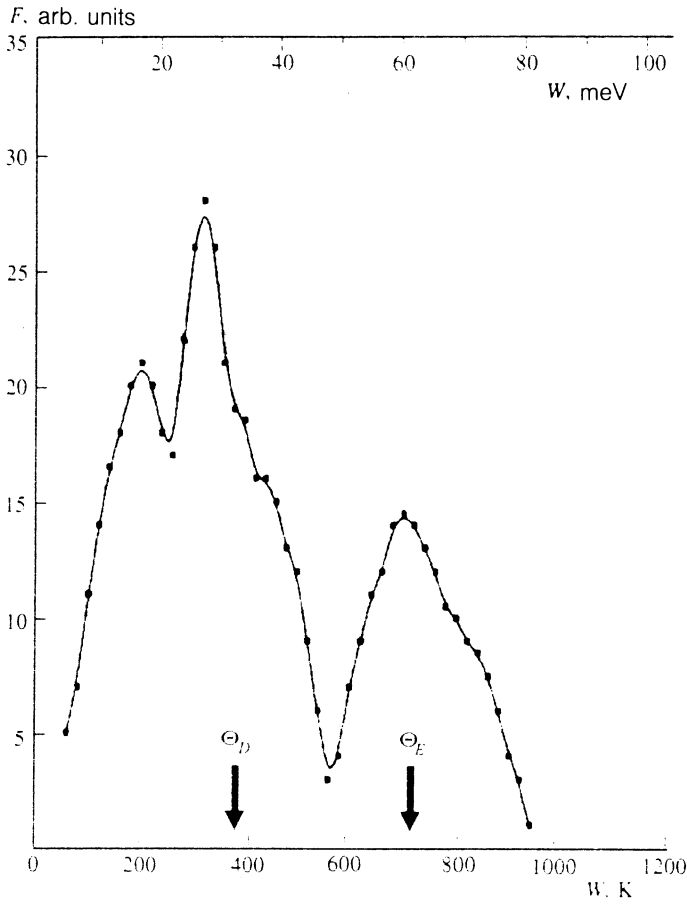FIG. 4. Density of phonon states in $Ba_{0.6}K_{0.4}BiO_3$.[7]

$Ba_{1-x}K_xBiO_3$ is divided into two parts separated by a region with a low density of states between 500 and 600 K (Fig. 4). The peak in the phonon density of states in the energy region above 600 K is associated with a breathing mode of the oxygen octahedra around Ba (or K) atoms. The density of states below 500 K is determined by acoustic phonons and libration modes of the BiO_6 octahedron. In this case it is natural to choose a model phonon spectrum in the form of an acoustic branch with a Debye dispersion law characterized by the Debye temperature Θ_D and a narrow optical-phonon peak a large distance away from this branch, characterized by an Einstein temperature Θ_E.

Following Ref. 13, we analyzed the function $\rho(T)$ using this model phonon spectrum. Assuming the correctness of Mattheisen's rule, the electrical resistivity of a metal can be written in the form of a sum $\rho(T)=\rho_0+\rho_f(T)$, where ρ_0 is a residual resistance that is temperature-independent and $\rho_f(T)$ is the temperature-dependent portion of the resistivity, which is determined by the scattering of electrons by phonons. The value of $\rho_f(T)$ is given by the expression[14]

$$\rho_f=C\int_0^\infty \alpha_T^2 F(\omega)f(\hbar\omega/kT)d\omega, \qquad (1)$$

where $F(\omega)$ is the phonon density of states, the statistical factor $f(x)=x(e^x-1)^{-1}(1-e^{-x})^{-1}$, and α_T^2 is a transport function which characterizes the electron–phonon in-

teraction. This last quantity differs from α^2, i.e., the square of the matrix element for the electron–phonon interaction entering into the expression for λ (where λ is the electron–phonon interaction constant), only by a factor that takes into account the scattering angle of an electron. The constant c is determined by the optical mass of an electron and the concentration of charge carriers, and cannot be computed exactly.

Substituting the density of states of the Debye spectrum, which describes the acoustic phonons very well, into the expression for $\rho_f(T)$ we obtain the Bloch–Grüneisen law for the temperature dependence of the electrical resistivity

$$\rho_{ac}(T,\Theta_D)=A_{ac}(T/\Theta_D)^4T\int_0^{\Theta_D/T} x^5(e^x-1)^{-1}$$

$$\times(1-e^{-x})^{-1}dx.$$

If, however, the phonon spectrum is Einsteinian, i.e., there is a local peak due to optical phonons, then the function $\rho_f(T)$ can be written in the form

$$\rho_{op}(T,\Theta_E)=A_{op}\Theta_E^2/T[\exp(\Theta_E/T)-1]^{-1}$$

$$\times[1-\exp(-\Theta_E/T)]^{-1}.$$

When both an acoustic branch and an optical peak that is far away in frequency are present in the phonon spectrum, the function $\rho(T)$ can be written in the form of a sum

$$\rho_f(T) = \rho_{\mathrm{ac}}(T,\Theta_\mathrm{D}) + \rho_{\mathrm{op}}(T,\Theta_\mathrm{E}),$$

where $\rho_{\mathrm{ac}}(T,\Theta_\mathrm{D})$ is determined by scattering of electrons by acoustic phonons, and $\rho_{\mathrm{op}}(T,\Theta_\mathrm{E})$ is determined by optical phonon scattering:

$$\rho_{\mathrm{ac}}(T) = C \int_0^{\omega_c} \alpha_T^2 F(\omega) f(\hbar\omega/kT) d\omega,$$

$$\rho_{\mathrm{op}}(T) = C \int_{\omega_c}^{\infty} \alpha_T^2 F(\omega) f(\hbar\omega/kT) d\omega,$$

$$k\Theta_\mathrm{D} < \hbar\omega_c < k\Theta_\mathrm{E}.$$

By approximating the experimental function $\rho(T)$ with the function

$$\rho(T,\Theta_\mathrm{D},\Theta_\mathrm{E}) = \rho_0 + \rho_{\mathrm{ac}}(T,\Theta_\mathrm{D}) + \rho_{\mathrm{op}}(T,\Theta_\mathrm{E})$$

$$= \rho_0 + 4A_{\mathrm{ac}}(T/\Theta_\mathrm{D})^4 T \int_0^{\Theta_\mathrm{D}/T} x^5 (e^x$$

$$-1)^{-1}(1-e^{-x})^{-1} dx$$

$$+ A_{\mathrm{op}}\Theta_\mathrm{E}^2 T^{-1}[\exp(\Theta_\mathrm{E}/T)-1]^{-1}[1$$

$$-\exp(-\Theta_\mathrm{E}/T)]^{-1},$$

in the best possible way, we can determine A_{ac}, Θ_D, A_{op}, and Θ_E. The approximation procedure was as follows. For certain prechosen values of Θ_D and Θ_E, optimal values of the parameters ρ_0, A_{ac}, and A_{op} were determined by the method of least squares, and the sum of squared deviations was calculated:

$$\Sigma = \sum_{i=1}^N [\rho(T_i) - \rho_0 - \rho_{\mathrm{ac}}(A_{\mathrm{ac}},T_i,\Theta_\mathrm{D})$$

$$- \rho_{\mathrm{op}}(A_{\mathrm{op}},T_i,\Theta_\mathrm{E})]^2.$$

This calculation was then repeated for other values of Θ_D and Θ_E, until values of Θ_D and Θ_E were found that correspond to a minimum of Σ. The step size for changing Θ_D and Θ_E was 10 K. The curves were calculated using 63 points.

The best agreement between the computed results and the experimental function $\rho(T)$ was observed for $\Theta_\mathrm{D} = 320$ K and $\Theta_\mathrm{E} = 680$ K. These values of Θ_D and Θ_E, which are indicated by arrows in Fig. 4, correlate well with the phonon spectrum of $Ba_{1-x}K_xBiO_3$ determined from neutron studies.[6,7] Figure 5a shows the results of our approximation of $\rho(T)$ along with the experimental data. The contributions to the resistivity due to scattering of electrons by acoustic and optical phonons are shown separately (Fig. 5b). Thus, by using a simple model of the spectrum consisting of an acoustic branch with a Debye dispersion law and an Einstein optical-phonon peak, and the three adjustable parameters Θ_D, Θ_E, and the ratio $A_{\mathrm{op}}/A_{\mathrm{ac}}$ of the contributions of optical and acoustic phonons to the electrical resistivity, we have succeeded in obtaining a function $\rho(T)$ that describes the experimental data quite well over the entire temperature range. For comparison we show in Fig. 6 the results of an analogous approximation using a phonon spectrum with one branch, either acoustic or optical.
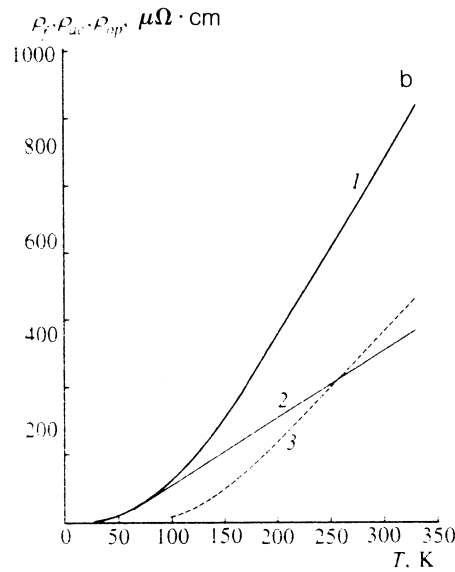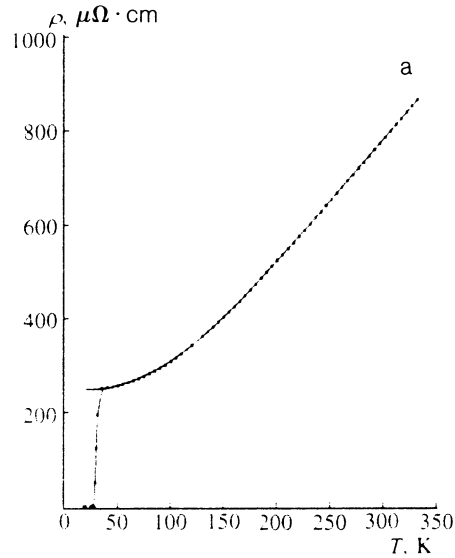

FIG. 5. (a) Temperature dependence of the resistivity in single crystals of $Ba_{0.6}K_{0.4}BiO_3$ (■—experimental data, (—)—approximation of the experimental data by the function $\rho(T,\Theta_\mathrm{D},\Theta_\mathrm{E}) = \rho_0 + \rho_{\mathrm{ac}}(T,\Theta_\mathrm{D}) + \rho_{\mathrm{op}}(T,\Theta_\mathrm{E})$, $\Theta_\mathrm{D} = 320$ K, $\Theta_\mathrm{E} = 680$ K. (b) Temperature dependence of the phonon part of the resistivity ρ_f in single crystals of $Ba_{0.6}K_{0.4}BiO_3$: (—)—approximation of the experimental data by the function $(\rho_{\mathrm{ac}}(T,\Theta_\mathrm{D}) + \rho_{\mathrm{op}}(T,\Theta_\mathrm{E}))$, $\Theta_\mathrm{D} = 320$ K, $\Theta_\mathrm{E} = 680$ K; (·····)—$\rho_{\mathrm{ac}}(T,\Theta_\mathrm{D})$, $\Theta_\mathrm{D} = 320$ K, the contribution of acoustic phonons to the resistivity; (----)—$\rho_{\mathrm{op}}(T,\Theta_\mathrm{E})$, $\Theta_\mathrm{E} = 680$ K, the contribution of optical phonons to the resistivity.

The values of Θ_D and Θ_E that correspond to the best approximations equal 570 and 880 K respectively. It is apparent that the approximation of $\rho(T)$ using a single acoustic branch is relatively accurate for this scale of the figure. However, the following facts are noteworthy: first of all, in this case the characteristic phonon energy $\Theta_\mathrm{D} = 570$ K is very close to the minimum in the phonon density of states for the spectrum of $Ba_{1-x}K_xBiO_3$ (Fig. 4); and secondly, the value of Θ_D determined by analyzing $\rho(T)$ us-
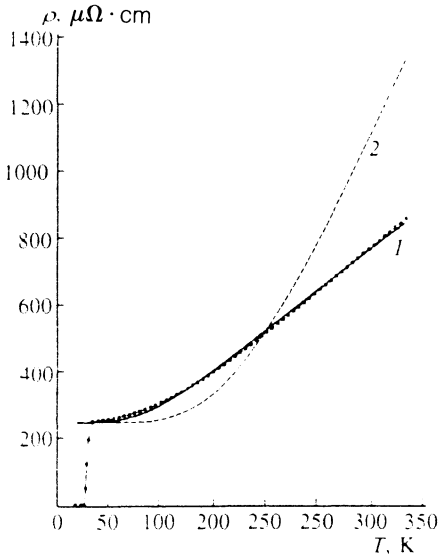
ing a spectrum consisting of an acoustic branch alone depends very strongly on the temperature range over which the approximation is carried out, changing from 300 to 570 K as the range under study increases from 150 to 330 K. In contrast, the values of the characteristic frequencies $\Theta_D=320$ K and $\Theta_E=680$ K for the two-branch spectrum are stable with respect to changes in the temperature range under study.

The expression for the electron–phonon interaction constant λ characterizing the superconducting properties of traditional superconductors, $\lambda=2\int_0^\infty\alpha^2F(\omega)\omega^{-1}d\omega$ is very reminiscent of Eq. (1) for $\rho_f(T)$. At high temperatures the statistical factor in the expression for $\rho_f(T)$ behaves as

$$f(\hbar\omega/kT)\mid_{T\to\infty}\to(kT/\hbar\omega)$$

and

$$\rho_f(T)\mid_{T\to\infty}\to C\int_0^\infty\alpha_T^2F(\omega)(kT/\hbar\omega)d\omega$$

$$=C'\lambda^TT$$

$$\approx C'\lambda T,$$

i.e. at $T\to\infty\,\rho f(T)\propto\lambda$.

By analogy with $\rho_f(T)$, the constant λ can be divided into two terms, i.e., $\lambda=\lambda_{ac}+\lambda_{op}$, that are determined by the interaction between electrons and acoustic and optical phonons respectively: $\lambda_{ac}=2\int_0^{\omega_C}\alpha^2F(\omega)d\omega/\omega$ and $\lambda_{op}=2\int_{\omega_C}^\infty\alpha^2F(\omega)d\omega/\omega$. Then $\rho_{ac,op}(T)\mid_{T\to\infty}\propto\lambda_{ac,op}$ and $\lambda_{ac}/\lambda_{op}=\rho_{ac}(T)/\rho_{op}(T)\mid_{T\to\infty}=A_{ac}/A_{op}$.

Thus, by taking the ratio of asymptotic forms of the resistivity functions, i.e., $\rho_{op}(T)/\rho_{ac}(T)\mid_{T\to\infty}$, we can determine the relative contribution of acoustic and optical

phonons to the electron–phonon interaction constant; for $Ba_{1-x}K_xBiO_3$ we have $\lambda_{op}/\lambda_{ac}=1.57$. Our lack of knowledge of the constant c in the equation for $\rho_f(T)$ prevents us from determining absolute values of λ_{ac} and λ_{op}. However, if we assume that the mechanism for superconductivity in $Ba_{1-x}K_xBiO_3$ is exclusively electron–phonon in nature, and take T_c for the superconducting transition from experiment, then λ_{ac} and λ_{op} can be calculated from the relation that connects T_c, Θ_D, Θ_E, and λ. In this case we make use of the Allen–Dynes formula, which gives T_c for superconductors with intermediate coupling:[15]

$$T_C=\frac{\omega_{\log}}{1.2}f_1f_2\exp\left(-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1-0.62\lambda)}\right),$$

$$f_1=1+\lambda^{4/3}(2.46+9.35\mu^*)^{1/2};$$

$$f_2=1+\frac{(\omega_2/\omega_{\log}-1)\lambda^2}{\lambda^2(1.82+11.5\mu^*)^2(\omega_2/\omega_{\log})^2},$$

$$\omega_2=\left[\int_0^\infty\alpha^2F(\omega)\omega d\omega\bigg/\left(\int_0^\infty\alpha^2F(\omega)\omega^{-1}d\omega\right)\right]^{1/2},$$

$$\omega_{\log}=\exp\left[\frac{2}{\lambda}\int_0^\infty\alpha^2F(\omega)\omega^{-1}\ln(\omega)d\omega\right],$$

where μ^* is assumed to equal 0.1.

The results we obtain are: $\lambda=0.98$, $\lambda_{ac}=0.38$, $\lambda_{op}=0.6$.

Thus, the experimental dependence of $\rho(T)$ in $Ba_{1-x}K_xBiO_3$ can be explained within the framework of the classical model of the electron–phonon interaction by using a phonon spectrum that consists of two branches: an acoustic branch with a Debye dispersion law and a Debye temperature $\Theta_D=320$ K, and an optical-phonon branch in the form of an Einstein peak with $\Theta_E=680$ K. In this case we find that the electrons interact strongly with optical phonons, and that the contribution of the optical phonons to the electron scattering, and, consequently, to the electrical resistance at high temperatures, is large compared to the contribution from acoustic phonons. Accordingly, the optical phonons contribute significantly to the electron–phonon interaction constant λ, which determines the superconducting properties of $Ba_{1-x}K_xBiO_3$, since $\lambda_{op}/\lambda_{ac}=1.57$. Under the assumption that the superconducting properties of $Ba_{1-x}K_xBiO_3$ arise purely from electron–phonon interactions, we have determined the constants λ, λ_{ac}, and λ_{op}.

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Translated by Frank J. Crowne