Dependence of the low-temperature specific heat of $RBa_2Cu_3O_x$ ceramics on the nature of the rare-earth ion R

N. V. Anshukova, Yu. V. Bugoslavskiĭ, V. G. Veselago, A. I. Golovashkin, O. V. Ershov, I. A. Zaĭtsev, O. M. Ivanenko, A. A. Kordyuk, A. A. Minakov, and K. V. Mitsen

Institute of General Physics, Academy of Sciences of the USSR

(Submitted 16 June 1988)

Pis'ma Zh. Eksp. Teor. Fiz. **48**, No. 3, 152–154 (10 August 1988)

That component of the low-temperature specific heat of the high-temperature superconductors which is linear in the temperature has been found to be highly sensitive to a substitution of magnetic rare-earth ions for nonmagnetic *Y*. The low-temperature anomaly in the phonon specific heat is described by a model of a uniaxial crystal.

It has been observed[1–3] that the low-temperature specific heat $C = \gamma T + BT^3 + \cdots$ of the high-temperature superconductors $YBa_2Cu_3O_{6.5+\delta}$ has a significant component which is linear in the temperature T. The value of γ depends on δ, as was shown in Ref. 3, and has a value $\sim$5–20 mJ/(mole·K^2), exceeding the electron component of the specific heat of normal metals. Such a temperature dependence of the specific heat is not characteristic of ordinary superconductors, for which the electron component of the low-temperature specific heat is exponentially small in the superconducting state. The presence of such a component in the specific heat of a high-temperature superconductor might be explained on the basis that the sample contains an uncontrollable nonsuperconducting phase in a concentration $\sim 1\%$ with a value of γ a hundred times that of normal metals. However, the very fact that a substance with such a large value of γ exists requires explanation.

In contrast, Anderson *et al.*[4] have explained this temperature dependence of the specific heat in terms of the presence of "spinons"—quasiparticles with a spin of 1/2 and no charge, i.e., fermions—in the high-temperature superconductors. These fermions might interact with magnetic impurities through dipole or exchange interactions, with the further consequence that the effective mass of the spinons and thus the value of γ might depend on the concentration of these impurities. One might expect that the value of γ in the high-temperature superconductors would depend on a substitution of magnetic rare-earth ions for nonmagnetic Y. The specific heat of ceramic high-temperature superconductors with various magnetic rare-earth ions was studied in Refs. 5–7. Those studies focused on the anomalies in the specific heat near the temperature at which the samples undergo a transition to an antiferromagnetic state, T_N. An anomaly in the phonon specific heat of $GdBa_2Cu_3O_x$ samples at $T = 20$–25 K was studied in Ref. 8. Similar anomalies were noted in Ref. 2 in a study of $YBa_2Cu_3O_x$ and $La_{1.85}Sr_{0.15}CuO_4$ samples.

In the present study we have found a method to describe this anomaly, by taking account of the anisotropy of the crystal lattice of the high-temperature superconductors. By singling out the component of $C(T)$ which is linear in the temperature we have studied the effect of the substitution of magnetic rare-earth ions for nonmagnetic Y on the value of γ in ceramic $RBa_2Cu_3O_{6.5+\delta}$ samples with R = Y, Gd, Ho, Tm, and Yb.

The specific heat was measured with the modulation microalorimeter of Ref. 9 as the temperature was raised linearly at a rate of 0.1–1 K/min. The amplitude of the modulation of the sample temperature was varied over the range 10^{-3}–10^{-1} K at modulation frequencies of 10–60 Hz and at temperatures of 3–30 K. The specific heat of the microsubstrate of the sample was 10^{-6}–5×10^{-4} J/K at 3–100 K; this value was taken into account in the measurements. The absolute error in the measurements of the specific heat did not exceed 5%, and the relative error did not exceed ~1%. The test samples, weighing ~10 mgf, were disks 3 mm in diameter and 0.3 mm thick. An x-ray structural analysis verified that the samples, synthesized by the standard procedure involving a sintering of oxides of the corresponding substances, were of a single phase, within ~1–2%. All of the test samples with $T_c = 91$–94 K and with a superconducting transition width $\Delta T \sim 1$–2 K exhibited a jump in the specific heat, $\Delta C/C \approx 2.5\%$, at T_c. The temperatures T_c and the widths ΔT were found from the temperature dependence of the specific heat, the diamagnetic moment, and the real and imaginary parts of the dynamic magnetic susceptibility.

Figure 1 shows the results of these measurements, as a plot of C/T versus T^2. In addition to the low-temperature magnetic component C_m, the specific heat C is seen to have a significant component which is linear in T; the coefficient of this component, γ, is found from the ordinate intercept in the limit $T \rightarrow 0$. The value of C_m is large near the magnetic transition temperature and falls off rapidly with increasing T. For the

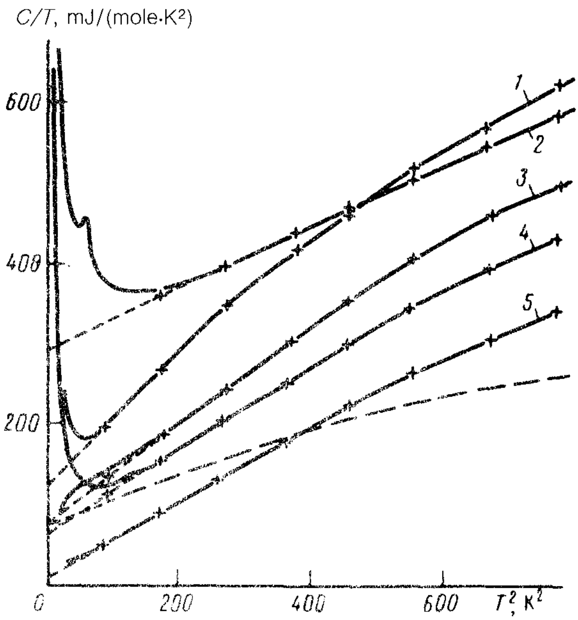

FIG. 1. Temperature dependence of the specific heat of $RBa_2Cu_3O_{6.5+\delta}$ samples with $\delta \approx 0.5$ and R = (1) Yb, (2) Ho, (3) Tm, (4) Gd, and (5) Y. The plus signs are theoretical values of the specific heat calculated from expression (1). The dashed line shows the temperature dependence of the specific heat of $BaCuO_2$ samples.

gadolinium samples, for example, the transition temperatures[5–8] $T_N = 2.2$ K, and at $T > 10$ K the dependence of $C/T = \gamma + BT^2 + C_m/T$ on T^2 is linear; i.e., the component C_m is negligible at these temperatures. With a further increase in the temperature, we observe a change in the slope of the plot of C/T versus T^2, which is particularly noticeable for the Yb and Tm samples. It turns out that the model of a uniaxial crystal, for which the elasticity along the long axis of the crystal lattice is considerably lower than that in the plane perpendicular to this axis, is a good approximation for describing the phonon specific heat of these samples. This observation means that the lattice is easily deformed in a relative displacement of the layers perpendicular to this axis; i.e., for transverse vibrations which are propagating along the axis the sound velocity ($v_\parallel$) is at its lowest, and in direction perpendicular to this axis the sound velocity ($v_\perp$) is considerably higher. In this connection we can introduce two Debye temperatures, $\Theta_1 = \hbar v_\parallel \pi c^{-1} k^{-1}$ and $\Theta_2 = \hbar v_\perp 2\sqrt{\pi} a^{-1} k^{-1}$, where k and $\hbar$ are the Boltzmann constant and Planck's constant, c and a are the lattice constants along and perpendicular to the long axis ($c \approx 3a$), and $\Theta_1 \ll \Theta_2$. At $T < \Theta_1$, vibrations with wave vectors $\mathbf{q}$ inside the ellipsoid $q_\parallel^2 v_\parallel^2 + q_\perp^2 v_\perp^2 = (kT/\hbar)^2$, are excited, while at $T > \Theta_1$ the wave vectors of the vibrations which are excited are within a disk of height $2\pi/s$ and radius $q_\perp = kT/\hbar v_\parallel$. The specific heat corresponding to the transverse vibrations is conveniently written as the sum of two integrals over these two regions. To describe the low-temperature specific heat associated with the longitudinal vibrations, we restrict the discussion to the isotropic approximation, introducing a Debye temperature Θ_3. It can be shown that we have $\Theta_3 \sim \Theta_2 \gg \Theta_1$, since the longitudinal vibrations are always coupled with the strains in all three directions. The phonon specific heat of a high-temperature superconductor can thus be written in the form

$$C_{\rm ph} = pR_0\left\{4\left[\frac{T^3}{\Theta_1\Theta_2^2}F(z_1) + \frac{T^2}{\Theta_2^2}(\phi(z_2) - \phi(z_3))\right] + 3\left(\frac{T}{\Theta_3}\right)^2 F(z_4)\right\}, \qquad (1)$$

where $p = 13$ is the number of ions in the unit cell of $RBa_2Cu_3O_7$, R_0 is the gas constant, $F(z) = \int_0^z x^4 e^x (e^x - 1)^{-2} dx$, $\phi(z) = \int_0^z x^3 e^x (e^x - 1)^{-2} dx$, $z_1 = \Theta_1/T$, $z_2 = \Theta_2/T$, $z_3 = \sqrt{2/3}\,\Theta_1/T$, and $z_4 = \Theta_3/T$. From (1) we see that at $T \ll \Theta_1$ the first two terms provide a value $\sim T^3/\Theta_1\Theta_2^2$, while at $T \gg \Theta_1$ they provide a value $\sim T^2/\Theta_2^2$. At $T \gg \Theta_2$, Θ_3, the Dulong-Petit law holds: $C_{\rm ph} = 3pR_0$. Expression (1) has a slope change at $T_0 \sim \Theta_1/3.9$ in the plot of C/T versus T^2. We can thus find Θ_1 immediately from the experimental values of T_0. From Fig. 1 we see that the experimental behavior $C(T)$ agrees well with the values calculated for $\gamma T + C_{\rm ph}$ from (1) with $\Theta_1 = 90$, 83, 86, and 62 K; $\Theta_2 = 850$, 810, 740, and 515 K; $\Theta_3 = 295$, 299, 279, and 320 K; and $\gamma = 10$, 60, 70, and 100 mJ/mole·K^2) for the samples with R = Y, Gd, Tm, and Yb, respectively. Not conforming to this series are the results for the samples containing Ho, whose specific heat can be described by an isotropic model with a Debye temperature $\Theta = 404$ K and $\gamma = 290$ mJ/(mole·K^2).

In summary, the anomaly in the phonon specific heat of a high-temperature superconductor can be described well by the model of a uniaxial crystal, and this anomaly depends on the atomic number of the rare-earth ion. Knowing Θ_1 and Θ_2, we can estimate the anisotropy of the transverse sound velocity: $v_\perp/v_\parallel$

$= \sqrt{\pi}/2(a/c)\Theta_2/\Theta_1 \approx 2.5$–3 at $c/a = 3$. It turns out that the value of γ increases by a factor of tens when nonmagnetic Y is replaced by magnetic rare-earth ions. In order to explain the measured values of γ in terms of the presence of a $BaCuO_2$ phase in the samples (Fig. 1), we would be forced to assume that, $GdBa_2Cu_3O_x$, for example, the concentration of this phase is at least 40%, and in $HoBa_2Cu_3O_x$ at least 90%, in contradiction of the data from the x-ray structural analysis. The sensitivity of γ to the particular rare-earth ion can be explained by assuming that the γT component of the specific heat of the high-temperature superconductors stems from Anderson spinons[4] which are interacting with magnetization fluctuations of the rare-earth sublattice.

[1]N. E. Philips, R. A. Fisher, S. E. Lacy *et al.*, Jpn. J. Appl. Phys. **26**, Sup. 26-3, 1115 (1987).
[2]A. Junod, A. Bezinge, D. Cattani *et al.*, Jpn. J. Appl. Phys. **26**, Sup. 26-3, 1119 (1987).
[3]A. Matsushita, T. Oguchi, K. Kimura *et al.*, Jpn. J. Appl. Phys. **26**, L1953 (1987).
[4]P. W. Anderson, G. Baskaran, Z. Zou, and T. Hsu, Phys. Rev. Lett. **58**, 2790 (1987).
[5]S. E. Brown, J. D. Thompson, J. O. Willis *et al.*, Phys. Rev. B **36**, 2298 (1987).
[6]T. Kohara, Y. Oda, Y. Konori *et al.*, Jpn. J. Appl. Phys. **26**, L1672 (1987).
[7]A. P. Ramirez, L. F. Schneemeyer, and J. V. Waszczak, Phys. Rev. B **36**, 7145 (1987).
[8]M. E. Reeves, D. S. Gitrin, B. G. Pazol *et al.*, Phys. Rev. B **36**, 6915 (1987).
[9]O. V. Ershov, A. A. Minakov, and V. G. Veselago, Preprint No. 233, P. N. Lebedev Physics Institute, Academy of Sciences of the USSR, Moscow, 1983, p. 31.

Translated by Dave Parsons