PHYSICAL REVIEW B VOLUME 46, NUMBER 1 1 JULY 1992-I

Thermopower of $Bi_{2-x}Pb_xSr_2CaCu_2O_{8+\delta}$

C. R. Varoy and H. J. Trodahl
Physics Department, Victoria University of Wellington, P.O. Box 600, Wellington, New Zealand

R. G. Buckley
DSIR Physical Sciences, P.O. Box 31313, Lower Hutt, New Zealand

A. B. Kaiser
Physics Department, Victoria University of Wellington, P.O. Box 600, Wellington, New Zealand
and Max-Planck-Institut für Festkörperforschung, Postfach 80 06 65, 7000 Stuttgart 80, Germany

(Received 7 June 1991; revised manuscript received 13 February 1992)

We report resistivity and thermopower measurements on a series of Pb-substituted ceramic samples of $Bi_2Sr_2CaCu_2O_{8+\delta}$. The samples show an increase in their conductivity and a systematic fall to more negative values of thermopower as holes are added with the introduction of progressively more Pb or oxygen, trends held in common with other high-T_c superconductors. Furthermore, the thermopower falls linearly with increasing temperature in all of our samples, with the unusual property that it extrapolates to a large (typically > 5 μV/K) nonzero value at zero temperature. This offset value decreases dramatically as holes are added, whereas the linear slope shows a much weaker decrease. This temperature dependence can be fitted to a model in which the thermopower is strongly enhanced at low temperatures by the electron-phonon interaction.

I. INTRODUCTION

To understand fully and then exploit the high-T_c superconductors it is important to determine not only their superconducting but also their normal-state properties. Furthermore, the unusual normal-state transport behavior displayed by many of these compounds may hold clues concerning the nature of the superconductivity itself. Among these is the thermopower, which is generally acknowledged to depend sensitively on the *energy dependence* of the electron lifetime and density of states near the Fermi energy (E_F). It is thus a useful complement to the resistivity, which depends simply on the value of these parameters at E_F.

As is documented in a recent review paper,[1] the normal-state thermopower of the copper-oxide superconductors has been measured by many groups, though there is as yet no consensus regarding the explanation of the unusual behavior of this parameter. Its magnitude is generally a few μV/K, as would be expected for a conventional metal with the low carrier densities characteristic of these materials. Its sign is commonly, but not always, found to be positive, consistent with the charge carrier sign as determined by Hall-effect measurements for most of the high-T_c materials. (Note that the sign of the thermopower does not unambiguously determine the sign of the charge carriers.) It is, however, not even approximately proportional to temperature, as is expected and approximately found for conventional metals when the phonon drag peak is suppressed. Furthermore, there is variability in the behavior measured by different groups, presumably arising from variations in composition. In this paper we report measurements of the thermopower of a series of Pb-substituted samples of $Bi_2Sr_2CaCu_2O_{8+\delta}$, and we have found systematic trends with changes to the Pb and oxygen concentration. Using these ceramic samples of varying composition, we have been able to investigate the thermopower for a large range of hole concentrations.

The $Bi_2(Sr,Ca)_{n+1}Cu_nO_{2n+4+\delta}$ (Bi-Sr-Ca-Cu-O) superconductors form a homologous series as n increases, with the members $n=1,2,3$ having been identified as superconducting.[2] The $n=2$ member is readily prepared as single phase, and up to 20% of the Bi atoms in this compound can be replaced by Pb. In common with all the high-T_c materials, these compounds possess copper-oxide layers, in this case with n CuO_2 layers in each unit cell, separated by BiO bilayers. Unlike $YBa_2Cu_3O_{7-\delta}$ (Y-Ba-Cu-O), the Bi-Sr-Ca-Cu-O compounds do not have CuO chain structures with their severely variable oxygen stoichiometry. Nonetheless, they show a degree of variability in their oxygen stoichiometry, associated with the BiO bilayers, which affects their physical properties.[3,4]

The normal-state resistivity ρ of the Bi-Sr-Ca-Cu-O compounds is approximately linear in temperature, in common with all the high-T_c materials. The members of this particular series show a thermopower (S) which is also linear in temperature with a negative slope, near -0.03 $\mu V/K^2$ in all reported data.[1] The thermopower data reported by various groups thus lie along approximately parallel lines when plotted against temperature. In all cases the data extrapolate to a large (> 5 μV/K) positive value at 0 K. This particularly simple behavior is shared with the Tl-based high-T_c compounds. On the other hand, the thermopower of Y-Ba-Cu-O shows a range of more complicated temperature dependences, with less agreement among the data from different groups.[1,5–8] It has recently been suggested that the thermopower in Y-Ba-Cu-O is complicated by variations in the relative contributions from the CuO chains and the CuO_2 planes.[8]

There exists only one previous measurement[9] of the thermopower in the Pb-substituted version of $n=2$ Bi-Sr-Ca-Cu-O for $x=0.5$. The results showed the lowest values of the thermopower as yet reported in this series of compounds, starting at zero just above T_c, and thereafter falling at a typical rate ($-0.03\ \mu V/K^2$). The same paper reports measurements on an unsubstituted sample as well, with essentially the same results. We will show below that these low values are likely the result of the material being heavily loaded with oxygen. Measurements on Pb-substituted $n=3$ Bi-Sr-Ca-Cu-O (Refs. 10–12) also yield a thermopower decreasing as the temperature increases, with varying magnitudes above T_c.

II. EXPERIMENTAL DETAILS

The samples were prepared by direct reaction of analytical quality reagents, the oxides of copper(II), bismuth(III), and lead(II) and the nitrates of calcium and strontium, all carefully dried at 170 °C to desorb water before weighing. Six samples were prepared, with lead substitutions x ranging from 0.1 to 0.35. The Pb concentration x given below are those determined from the initial weighings, which were checked by EDAX and wet chemical analysis to be identical to the average values in the finished samples.

The stoichiometric mix was ground and fired at 750 °C to melt and thoroughly mix the reagents. The products were then reground in cyclohexane, dried, pressed into 25-mm pellets, and fired at 830 °C on gold foil in air for 4 h. Products from this reaction were again ground in cyclohexane, dried, pressed, and reacted at 830 °C in air for 12 h. This procedure was then repeated, after which the samples were annealed at 800 °C in air for 1 h and then quenched in liquid nitrogen. The samples were then subjected to x-ray diffractometry (XRD) and resistance measurements to establish that they were the required compound before regrinding them and pressing them into the $50\times4\times4$ mm^3 bars required for the transport measurements. The bars were reacted in air at 850 °C for 6 h, annealed in a flowing 2% O_2-98% N_2 mix for 1 h at 800 °C, and finally quenched in liquid nitrogen. The result of this final reaction procedure is to minimize the oxygen content and thus the hole concentration in the material.[3] We are unable to quote a value of δ for our samples, although we expect this parameter to be the same (δ_0) for all of the material prepared with the final reaction outlined above. The oxygen concentration in these materials can be reversibly altered by performing the final reaction and quenching in different atmospheres,[3] and as discussed below we have measured the thermopower on one of our samples annealed in enriched oxygen atmospheres. In this case we were able to measure the change in δ after the further reaction by noting the change in the weight of the sample.

12 mm-diam pellets were prepared at the same time as the transport bars, and these were used for XRD characterization. A representative pattern is shown in Fig. 1. The most obvious impurity phase, indicated by three closely spaced peaks near 35°, were reported by Lee *et al.*[13] to be $Bi_2O_3\cdot4(Ca_{1/3}Sr_{2/3})O$.

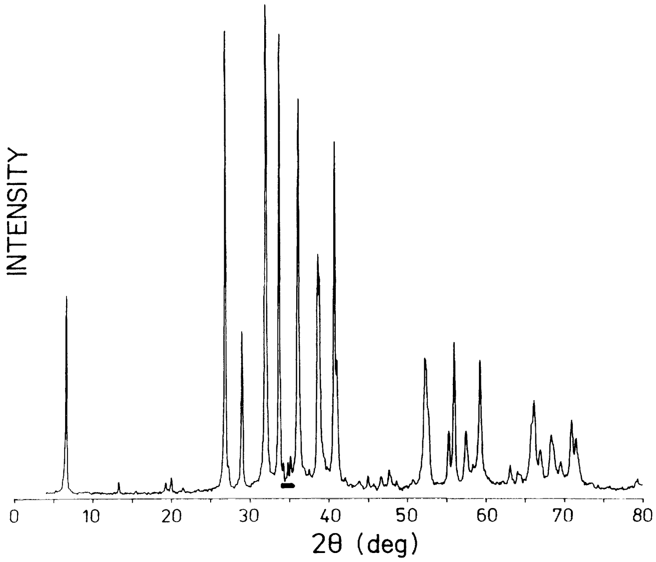

FIG. 1. A typical x-ray diffraction pattern. The only lines that cannot be indexed in the crystal structure of Bi-Sr-Ca-Cu-O are the three very small peaks near 35°, marked by a dark bar under the spectrum.

Resistivity measurements were made with the standard four-probe method, carefully reversing the current to correct for thermoelectric voltages. The thermopower was measured against manganin leads whose thermopower had been measured against pure Pb, assuming the absolute calibration of Roberts.[14] The data presented below have all been corrected for the contribution of manganin leads to the measured relative thermopower. The technique used here is similar to that in Refs. 5, 6, and 15 and the uncertainties are comparable to those described in those references. The resistivity data are accurate to 0.1 mΩ cm and the thermopower data to 0.3 $\mu V/K$. All temperature measurements were referenced to a calibrated Rh-Fe thermometer and are accurate to 0.5 K.

III. RESULTS AND DISCUSSION

The measured resistivities are shown in Fig. 2 for the samples where data are available up to room temperature. We note that, although T_c is only weakly dependent on Pb content, the normal-state resistivity drops and its temperature coefficient rises with the introduction of Pb. The relative insensitivity of T_c can be understood as a consequence of the well-documented parabolic maximum that this parameter shows for a hole concentration of 0.15 per Cu atom in CuO_2 planes.[16] As noted above, the preparation procedure we have used minimizes the oxygen, and thus the hole, concentration, with the result that our samples lie close to the maximum in T_c, on the low hole concentration side. The substitution of Pb^{2+} for Bi^{3+} then increases the hole concentration across the flat

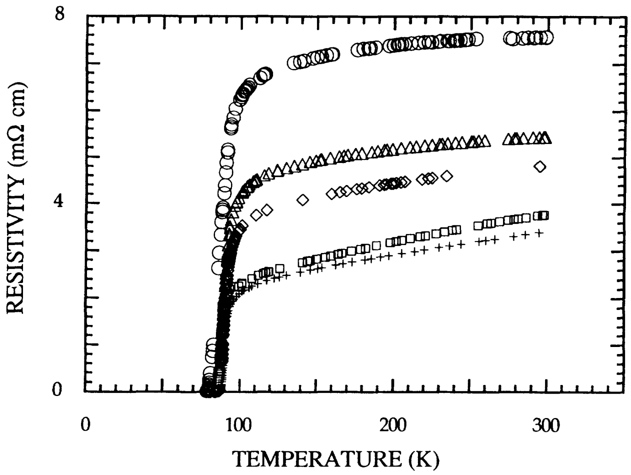

FIG. 2. The resistivity of samples with $\delta=\delta_0$ and x of 0.1 (circles), 0.15 (triangles), 0.2 (diamonds), 0.3 (+), and 0.35 (squares).

maximum region. Note that the lowest Pb concentration shows a reduced T_c, in agreement with this picture.

We turn now to the thermopower, shown in Fig. 3. Since its measurement does not rely on a knowledge of the form factor (L/A), the thermopower is less effected by the porosity of the sample than is the resistivity. Thus, the data shown represent an average between the c-axis and basal plane values, weighted by the respective conductivities. The basal plane conductivity is much the larger, so our measured thermopower approximates the basal plane value, S_{ab}.

The thermopower of Fig. 3 has, in all cases, a positive or very small negative value just above T_c and it falls linearly with a slope near $-0.03\ \mu V/K^2$ as the temperature rises toward 300 K. The magnitude of this slope varies by about 30%, being largest for samples with the most positive thermopower. There is a shift toward more negative values as Pb is added, i.e., as the hole concentration is increased. That it is the hole concentration which causes the drop is confirmed by the data displayed in Fig. 3(b) which show a similar drop when the hole concentration is increased by adding oxygen. This trend toward more negative values of thermopower with increasing oxygen concentration has also been reported for unsubstituted $n=2$ Bi-Sr-Ca-Cu-O.[17] Our results span the range of curves reported by other groups, and identifies the variation in earlier results as arising from variable hole concentration. The shift toward more negative values when adding positive charge carriers is also found in the more complicated thermopower of Y-Ba-Cu-O,[18] and in that case it has been attributed to changes in the balance of contributions to the thermopower from the CuO chains and the CuO_2 planes.[8] The same explanation obviously cannot be used in the present case. This behavior would also appear to be inconsistent with a picture in which the changes result simply from extra carriers appearing in a holelike conduction band unless the hole band thermopower itself is negative. A contribution to the thermopower that is of the opposite sign to that of the carriers can result, for example, from strong energy dependence in the carrier relaxation time or density of states.

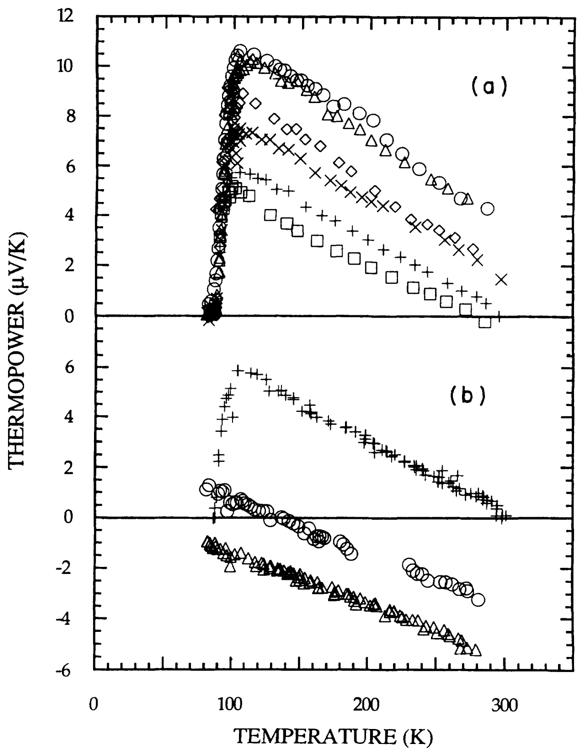

FIG. 3. (a) The thermopower of samples with $\delta=\delta_0$ and x of 0.1 (circles), 0.15 (triangles), 0.2 (diamonds), 0.25 (×), 0.3 (+), and 0.35 (squares). In the interest of clarity, the data points represent averages over typically five adjacent values. (b) The thermopower of the $x=0.3$ sample with different oxygen concentrations δ of δ_0 (+), $\delta_0+0.23$ (circles), and $\delta_0+0.27$ (triangles).

We now consider the detailed temperature dependence of the thermopower of Bi-Sr-Ca-Cu-O, displayed in Fig. 3. The most striking feature is that it retains its linearity over the entire temperature range measured. It is unlikely that such a simple linear thermopower would be an accidental artifact arising from a combination of diffusion and phonon drag effects. The fact that this pattern is systematically maintained as the magnitude of the thermopower is changed by the substitution of Pb or oxygen further consolidates this view. A linear temperature dependence in the thermopower is usually ascribed to a diffusion thermopower of a degenerate electron gas; however, such a contribution is normally proportional to the temperature, and thus should extrapolate to zero at 0 K.

Deviations from strict linearity can result from a nonlinear energy dependence in the conducting properties of electrons near the Fermi energy, and when this dependence is caused by the electron-phonon interaction[19] then at intermediate temperatures ($\Theta_D > T > \Theta_D/3$, where Θ_D is the Debye temperature) the thermopower approximates a linear behavior extrapolating to a nonzero value at 0 K. The effect results from distortions to the electron density of states at energies within Θ_D of E_F; the thermopower depends on the average derivatives within about kT of E_F which are then different for temperatures above and below Θ_D. This effect has been seen in many metallic systems with short electron and phonon mean free paths, which suppresses the phonon drag thermopower.[1,15,20,21] It is normally observed as an enhancement by the mass enhancement factor at low temperatures, and the apparent extrapolated offset is thus both modest and of the same sign as the slope, neither of which are characteristic of the data shown in Fig. 3. The conventional superconductor, Sn-Ag, does show an offset of opposite sign to the slope, however, and it is thus qualitatively similar to the Bi-Sr-Ca-Cu-O materials.[22] Furthermore, it has recently been pointed out that some aspects of the electronic behavior of the Bi- and Tl-based copper-oxide superconductors can be accounted for by a standard metallic model in which the electron-phonon interaction is greatly enhanced,[23] as might occur for strongly anharmonic phonons.[24,25] Within this scenario it is not unreasonable to consider the possibility of an anomalously strong electron-phonon enhancement in the diffusion thermopower of Bi-Sr-Ca-Cu-O.

With the inclusion of the enhancement, the diffusion thermopower can be written

$$S = S_b + c\lambda_S(T)T \ , \tag{1}$$

where S_b is the (bare) unenhanced thermopower, normally considered to be linear in temperature T, and $\lambda_S(T)$ is a function that is determined by an integral over the Eliashberg function $[\alpha^2F(E)]$ as defined in Ref. 19. $\lambda_S(0)$ is the usual mass enhancement factor and $\lambda_S(\infty)=0$. c is a constant which depends on the balance of thermopower contributions from different bands and their relative enhancement factors and can be of opposite sign to S_b if the contributions have opposite signs and very different enhancements.

In order to fit the data to Eq. (1), we have calculated $\lambda_S(T)$ using an Eliashberg function $\alpha^2F(E)$ of the same shape as the measured phonon density of modes $F(E)$ for $n=2$ Bi-Sr-Ca-Cu-O.[26] The bare thermopower was taken as linear. Examples of the resulting fits are shown as solid lines in Fig. 4. The values of S_b/T varied between -18 and -28 nV/K^2, tending to be of smaller magnitude for samples showing more negative thermopower, while the values of $c\lambda_S(0)$ varied from 182 nV/K^2 for $x=0.1$–11 nV/K^2 for the highly oxygenated $x=0.3$ sample. The large size of some of these values of $c\lambda_S(0)$, and the fact that they have the opposite sign to S_b, would require an anomalously strong electron-phonon interaction for some of the carriers contributing a positive thermopower.

The temperature dependence predicted by the enhancement model does not depend strongly on the details of the Eliashberg function, but rather on the energy range in which the major weight of the function is found. It is clear from Fig. 4 that an improved fit would be obtained if the predicted peak was shifted toward lower temperature, which occurs if $\alpha^2F(E)$ is weighted toward lower energy; i.e., if the carriers interact more strongly with lower-energy phonons. We therefore show by dashed lines in Fig. 4 fits to an Eliashberg function calculated for Y-Ba-Cu-O,[27] but used here only as a representative function with greater weight at lower energies. The use of this function shows an excellent description of the data.

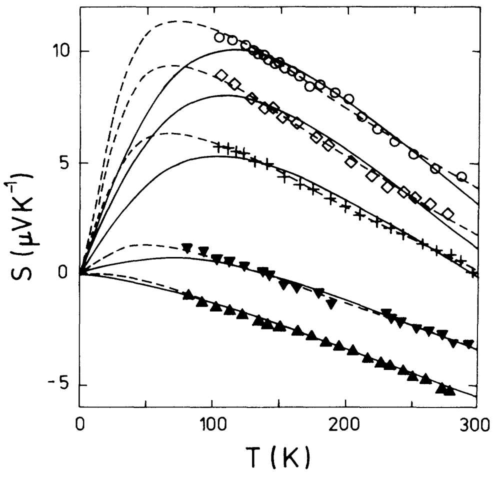

FIG. 4. A comparison of the measured thermopower with the calculated thermopower caused by a very strong electron-phonon interaction for samples with $\delta=\delta_0$ and $x=0.1$ (circles), 0.2 (diamonds), and 0.3 (+), and for the $x=0.3$ sample with $\delta=\delta_0+0.23$ (inverted triangles) and $\delta=\delta_0+0.27$ (upright triangles). The solid curves are for an Eliashberg function with the same phonon density of states as measured for $x=0$, and the dashed curves are for an Eliashberg function with greater weighting for lower-energy modes. Some data sets are omitted for clarity.

It is interesting to speculate whether the possible strong electron-phonon effect on the thermopower is related to the occurrence of a high T_c. In Fig. 5 we plot, as a function of the relative hole concentration, a linear extrapolation of the thermopower to 0 K and T_c determined by the zero-resistance temperature. Since there are two Cu atoms per unit cell, the excess hole concentration produced by adding Pb in $Bi_{2-x}Pb_xSr_2CaCu_2O_{8+\delta}$ is estimated as $x/2$ per Cu atom. The width of the superconducting transition increases as hole concentration is reduced, so the zero-resistance T_c does not give an adequate indication of the whole transition. For this reason, we also indicate in Fig. 5 the range over which the transition occurs by plotting an approximate measure of an upper "onset" temperature. It is not possible to define such an "onset" temperature precisely, but this is not important for our present qualitative comparison. Our "onset" temperature is taken as the intersection of lines drawn tangent to $R(T)$ at points well above T_c and at the center of the transition region. It indicates very approximately where portions of the sample first become superconducting as the temperature is reduced, although, of course, the effect of superconducting fluctuations in the normal state extends to higher temperatures. The uncertainty in estimating the quantities in Fig. 5 from the data is comparable to the size of the plotted symbols. The decreasing "onset" temperature with an increasing hole concentration is similar to the dependence shown by the

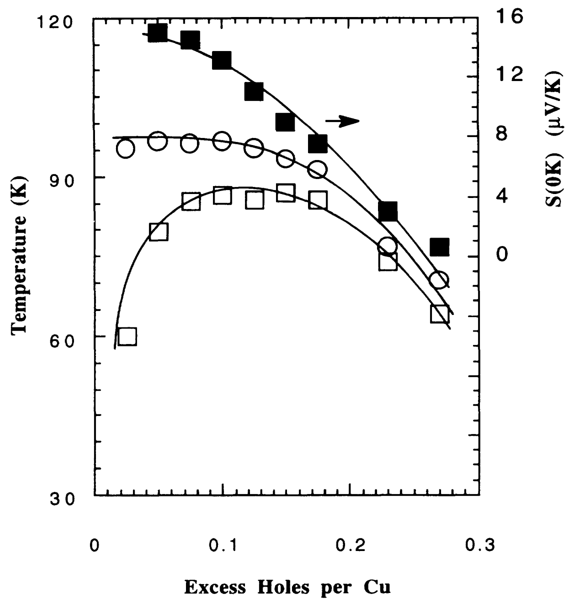

FIG. 5. The thermopower extrapolated to 0 K (solid squares), the zero-resistance temperature (open squares), and the "onset" transition temperature (open circles, see text for definition and discussion), plotted against the hole concentration expressed as a number of holes per Cu atom. The hole concentration is given relative to the concentration in material with $x=0$ and $\delta=\delta_0$.

oxygen isotope shift of T_c in Y-Ba-Cu-O (Refs. 28 and 29) and $La_{2-x}Sr_xCuO_4$.[30] The extrapolated thermopower $S(0)$ in Fig. 5, which depends in the model on the strength of the electron-phonon interaction and other electronic properties, displays a qualitatively similar dependence on hole concentration, suggesting the possibility that the origin of these variations may be related in some way. The variation of $S(0)$ is more similar to that of the approximate "onset" temperature we have defined than to the zero-resistance T_c, which decreases at low hole concentrations owing to the greater width of the transition.

IV. CONCLUSIONS

We have performed normal-state resistivity and thermopower measurements on a series of ceramic samples of $Bi_{2-x}Pb_xSr_2CaCu_2O_{8+\delta}$. The samples were seen to become more conductive as Pb was added, as is expected from the increase in the hole carrier density. The thermopower became more negative with an increase of holes caused by the introduction of Pb or excess oxygen, which is against the trend expected on a simple model unless the thermopower contributed by the holes is negative. It is interesting that the thermopower of Y-Ba-Cu-O shows a similar dependence on the hole concentration.

The temperature dependence of the thermopower retained the simple linear form already noted for pure $Bi_2Sr_2CaCu_2O_{8+\delta}$ over the entire range of Pb and oxygen substitutions. We suggest than an explanation of this particularly simple behavior may lead to an understanding of the transport properties in the high-T_c compounds. One possibility for the explanation is that the electron-photon interaction is particularly strong for some carriers, leading to a temperature dependence related to the electron-phonon effects already seen in metallic glasses and some conventional superconductors. A fit to such a model would require that the unenhanced thermopower shows only a weak variation with hole concentration, while the net electron-phonon effect (summed over different thermopower contributions) falls as holes are added to the compound. A complex model involving contributions of different sign from different parts of the Fermi surface would be needed to give this behavior.

---

[1] A. B. Kaiser and C. Uher, in *Studies of High Temperatures Superconductors,* edited by A. V. Narlikar (Nova, New York, 1991), Vol. 7, p. 353.

[2] J. L. Tallon, R. G. Buckley, P. W. Gilberd, M. R. Presland, I. W. M. Brown, M. E. Bowden, L. A. Christian, and R. Goguel, Nature **333**, 153 (1988).

[3] J. L. Tallon, R. G. Buckley, P. W. Gilberd, M. R. Presland, Physica C **158**, 247 (1989).

[4] R. G. Buckley, J. L. Tallon, I. W. M. Brown, M. R. Presland, N. E. Flower, P. W. Gilberd, M. Bowden, and N. B. Milestone, Physica C **156**, 629 (1988).

[5] A. Mawdsley, H. T. Trodahl, J. Tallon, J. Sarfati, and A. B. Kaiser, Nature **328**, 233 (1987); H. J. Trodahl and A. Mawdsley, Phys. Rev. B **36**, 8881 (1987).

[6] C. Uher and A. B. Kaiser, Phys. Rev. B **36**, 5680 (1987).

[7] U. Gottwick, R. Held, G. Sparn, F. Steglich, H. Rietschel, D. Ewert, B. Renker, W. Bauhofer, S. von Molnar, M. Wilhelm, and H. E. Hoenig, Europhys. Lett. **4**, 1183 (1987).

[8] J. L. Cohn, S. A. Wolf, V. Selvamanickam, and K. A. Salama, Phys. Rev. Lett. **66**, 1098 (1991).

[9] C. N. R. Rao, T. V. Ramakrishnan, and N. Kumar, Physica C **165**, 183 (1990).

[10] W. Lang, H. Jodlbauer, P. Schaffarich, H. Kuzmany, E. Bauer, and R. Hauser, in *Proceedings of the International Conference on Transport Properties of Superconductors, Rio de Janeiro, 1990,* edited by R. Nicolsky (World Scientific, Singapore, 1990), p. 631.

[11] Ch. Laurent, S. K. Papatis, S. M. Green, H. L. Luo, C. Politis, K. Durczewski, and M. Ausloos, Mod. Phys. Lett. B **3**, 241 (1989).

[12] M. Pekala, K. Pekala, M. A. Senaris-Rodriguez, F. Garcia-Alvarado, and E. Moran, Solid State Commun. **77**, 437 (1991).

[13] C. L. Lee, J. J. Chen, W. J. Wen, T. P. Peng, J. M. Wa, T. B. Wu, and T. S. Chin, J. Mater. Res. **5**, 1403 (1990).

[14] R. B. Roberts, Philos. Mag. **36**, 91 (1977).

[15] K. D. D. Rathnayaka, A. B. Kaiser, and H. J. Trodahl, Phys. Rev. B **33**, 889 (1986).

[16] M. R. Presland, J. L. Tallon, R. G. Buckley, R. S. Liu, and N. E. Flower, Physica C **176**, 95 (1991).

[17] M. F. Crommie, G. Briceno, and A. Zettl, Physica C **162-164**, 1397 (1989).

[18] H. Ishii, H. Sato, N. Kanazawa, H. Takagi, S. Uchida, K. Kitizawa, K. Kishio, K. Fueki, and S. Tanaka, Physica B **148**, 419 (1987).

[19] A. B. Kaiser, Phys. Rev. B **29**, 7088 (1984).

[20] M. A. Howson and B. L. Gallagher, Phys. Rep. **170**, 265 (1988).

[21] A. B. Kaiser, Phys. Rev. B **37**, 5924 (1988).

[22] E. Compans and F. Baumann, Jpn. J. Appl. Phys. **26-3**, 805 (1987).

[23] A. B. Kaiser and G. Mountjoy, Phys. Rev. B **43**, 6266 (1991).

[24] J. R. Hardy and J. W. Flocken, Phy. Rev. Lett. **60**, 2191 (1988).

[25] N. M. Plakida, V. L. Aksenov, and S. L. Drechsler, Europhys. Lett. **4**, 1309 (1987).

[26] W. Weber and L. F. Mattheiss, Phys. Rev. B **37**, 599 (1988).

[27] B. Renker, F. Gompf, D. Ewert, P. Adelmann, H. Schmidt, E. Gering, and H. Mutka, Z. Phys. B **77**, 65 (1989).

[28] J. P. Franck, J. Jung, M. A-K. Mohamed, S. Gygax, and G. I. Sprouel, Phys. Rev. B **44**, 5318 (1991).

[29] H. J. Bornemann and D. E. Morris, Phys. Rev. B **44**, 5322 (1991).

[30] M. K. Crawford, M. N. Kuncher, W. E. Farneth, E. McCarron III, and S. J. Poon, Phys. Rev. B **41**, 282 (1990).