Specific heat of Zn- and Co-substituted $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}M_x)_2O_y$

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The specific heat of several Zn- and Co-doped $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}M_x)_2O_y$ superconductors was investigated. Co substitution is paramagnetic, and introduces a linear term in C_p at low temperatures, without reduction in the specific-heat discontinuity $\Delta C_p/T_c$ at T_c. The results can be understood as gapless superconductivity in a highly anisotropic *s*-wave or *d*-wave superconductor. Zn substitution is nonmagnetic and does not lead to these phenomena.

Many investigations of the specific heat of cuprate high-T_c superconductors have given indications of a linear term in C_p at low temperatures.[1] This term is always found in superconductors incorporating barium, in particular in $YBa_2Cu_3O_7$ (YBCO), but also in other systems, e.g., $(La_{1-x}M_x)_2CuO_4$ with M = Sr or Ba. In contrast to this, most low-temperature specific-heat measurements on Bi-based superconductors (both 2:2:1:2 and 2:2:2:3) do not show this linear term.[1,2] There is no doubt that some of the linear contribution to C_p arises from impurity phases, in particular $Y_2Cu_2O_5$ and $BaCuO_2$. Particularly detailed studies of this question have been made by Phillips *et al.*[3] on $YBa_2Cu_3O_7$. In their work they separate the contribution to the concentration of Cu^{2+} moments in impurity phases from that present in the YBCO lattice. They establish a correlation between the amount of superconductivity in this lattice with the concentration of Cu^{2+} moments by comparing the specific-heat discontinuity at T_c with the observed linear term. It appears, that even in very good YBCO samples, some Cu^{2+} moments are present. This concentration can be rapidly increased by substitution of Zn for Cu, apparently without reduction in T_c. It is believed that Cu^{2+} present on the YBCO lattice locally quenches superconductivity (within a coherence volume), and that the linear term arises from the specific heat of these normal regions. The absence of the linear term in Bi-based superconductors is apparently due to much lower concentrations of Cu^{2+} spins.[2]

In the present work we decided to study a system which does not show a linear term initially, and investigate whether substitution for copper can produce such a term. We studied the system $Bi_{1.8}Pb_{0.2}Sr_2CaCu_2O_y$, and substituted Zn and Co for Cu.

Two groups of samples were made, of composition $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}M_x)_2O_y$, where M = Zn or Co, including an unsubstituted sample. For Zn substitution we investigated the concentrations $x = 0.02$ and 0.04, and for Co substitution $x = 0.02$, 0.03, 0.04, 0.06, and 0.08. The initial reagents were Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, CuO, ZnO, and $Co_{2.835}O_4$ and purity levels were 99.99% or better. The cobalt oxide is nonstoichiometric, and the actual cobalt to oxygen ratio was obtained by analysis. The samples were prepared by the solid-state reaction method, using identical procedures at all concentrations. The ground and pressed powder mixtures were calcined in air for 48 h at 800 °C with four intermediate grindings. Subsequently, the samples were sintered at 860 °C in air for 90 h, and slowly cooled to room temperature. The samples were investigated by x-ray-powder diffraction (Cu $K\alpha$). For all samples, with the exception of the 6 and 8 % Co samples, the x-ray patterns can be indexed completely with the 2:2:1:2 phase of Bi-Sr-Ca-Cu oxide (BSCCO). In Fig. 1 we show the powder-x-ray spectrum at low angles. The reflections (002) occur at $2\Theta = 5.7°$ for the 2:2:1:2 phase, and at 4.7° for the 2:2:2:3 phase, and 7.1 to 7.2° for the 2:2:0:1 phase. No evidence for either the 2:2:2:3 or 2:2:0:1 phase is therefore present. For the 6 and 8 % Co samples we see an impurity peak at 7.4°; this is the nonsuperconducting "$Sr_2Bi_2CuO_6$" phase,[4] with an estimated abundance of about 6% of the major phase. We find that Co substitution reduces the *c*-axis parameter from about 30.90 Å to 30.74 Å, or about 0.5%; this is shown in Fig. 2.

The samples were characterized further by resistance and dc-magnetization measurements. We find that the transitions remain reasonably sharp; resistive transition widths (10–90 %) are 2.8 K (0% Co), 3.3 K (2% Co), 4.9 K (3% Co), 5.3 K (4% Co), 8.1 K (6% Co), and 11.5 K (8% Co). The transition temperature decreases with Zn and Co substitution. The decrease in T_c for Zn is much smaller, and stops at $x = 0.04$, which may be due to solution limits.[5] For Co substitution we find a monotonic decrease of T_c with Co concentration. Transition temperatures obtained magnetically are given in Table I. Meissner fractions were obtained from the low-temperature field-cooled susceptibility (at 2 G), compared to the ideal value of $\frac{1}{4}\pi$.

The magnetic susceptibility in the normal state was also obtained, it is shown in Fig. 3, and was analyzed in terms of the Curie relation

$$\chi(T) = \chi_0 + C/T \ . \tag{1}$$

Zn doping barely changes the susceptibility of the normal state, and it tends to decrease with x. For Co-doped samples, the normal-state susceptibility increases rapidly and

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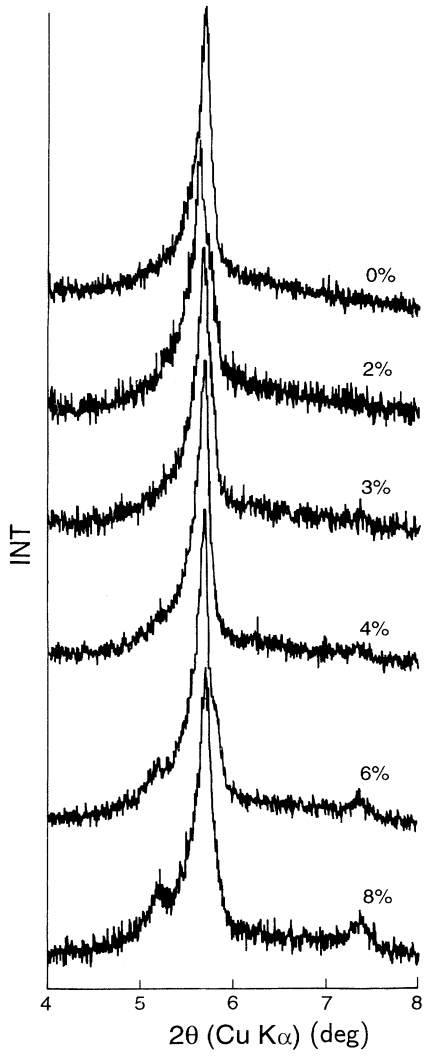

FIG. 1. X-ray-powder spectrum (Cu $K\alpha$) at low angles for the samples of $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}Co_x)_2O_y$, showing the (002) reflection of Bi 2:2:1:2. The Co concentrations x are shown.

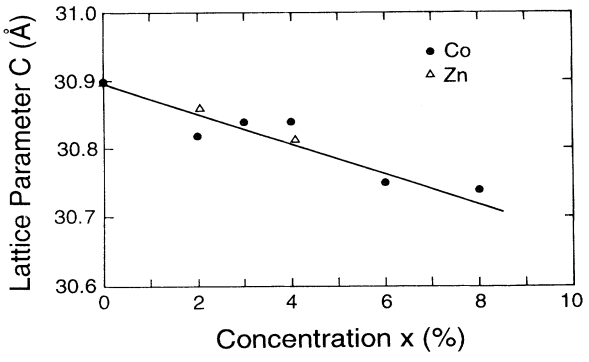

FIG. 2. The c-axis parameter from x-ray-powder diffraction as a function of substitution level for Zn- and Co-substituted $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}M_x)_2O_y$.

TABLE I. Characteristic data for $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}M_x)_2O_y$ samples with M = Zn or Co substitution.

Substit.	x (%)	Meissner fraction $\lvert 4\pi\chi_{FC}\rvert$	$T_{c,mag}$ (K)	Curie const C 10^{-3} emu K/mol	A 10^{-2} JK/mol	γ_0 mJ/mol K^2	θ_0 (K)	m J/mol K	θ_E (K)	T_c (K)	$\Delta C_p/T_c$[a] mJ/mol K^2
0	0	0.27	77.1	4.13±0.12	4.8±2	0±2	265±3	7.2±0.7	61		
Zn	2		72.4	0.91±0.04	2.7±2	0.3±2	251±4	4.8±0.6	56		
Zn	4		65.1	4.79±0.32	1.8±2	0±1.8	252±2	9.3±0.7	66		
Co	2	0.26	50.7	71.0±0.4	21±4	12.6±1.7	247±2	4.6±0.6	65	51.2	67
Co	3	0.25	48.6	100±1	12±3	15.6±1.9	243±3	5.1±0.4	58	46.0	36
Co	4	0.24	43.0	118±1	1.7±4	24.7±1.2	255±2	5.5±0.4	64	44.2	55
Co	6	0.20	38.8	154±1	5.7±3	18.3±2.4	245±3	2.2±0.7	62	39.0	54
Co	8	0.18	35.8	188±1	4.1±2	18.4±1.4	252±2	4.5±0.5	65	35.1	59

[a]Uncertainties in $\Delta C_p/T_c$ are about ±35%.

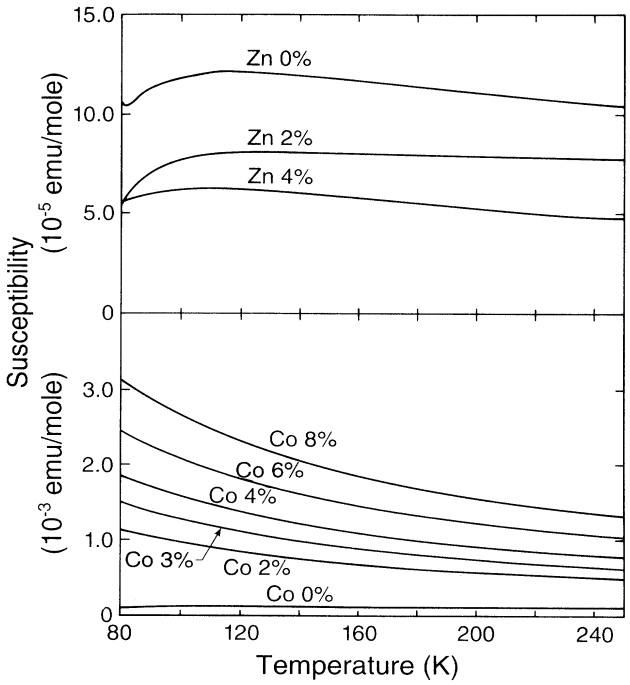

FIG. 3. The magnetic susceptibility in the normal state for Zn- and Co-substituted $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}M_x)_2O_y$.

monotonically with increasing x. In Table I and Fig. 6, we give the value of the Curie constant for each sample obtained by least-squares fit.

The specific heat of all samples was measured in an adiabatic calorimeter, using the heat-pulse method. Sample sizes of about 2 g were used. In Fig. 4 we present the low-temperature data for the Co-substituted samples. The specific-heat data in the range 2–10 K were fit by the expression

$$C_p(T)=AT^{-2}+\gamma_0 T+\beta T^3+mC_E(T)\ . \qquad (2)$$

The AT^{-2} term represents the low-temperature upturn usually observed, it is believed to be the high-temperature part of a Schottky anomaly. $\gamma_0 T$ is the linear term, if present and βT^3 is the lattice term. The last term represents an Einstein term, which we observe in all our samples. The term is particularly visible in plots of C_p/T^3 vs T. This term is now believed to be associated with low-lying near-dispersionless optical modes.[6] In Table I we include the values for the various constants in Eq. (2) obtained by least-squares fitting, as well as the low-temperature Debye temperature obtained from the T^3 term. The Einstein term is almost unchanged. The Debye temperature is on average about 6% less in the substituted samples. We see from Table I, that Zn substitution does not introduce a linear term, although the transition temperature has decreased. In contrast to this, Co doping even at the lowest levels investigated (2%) immediately introduces a linear term. This term increases up to 4% Co and then essentially stays constant.

We are now turning to the region near T_c, the data are shown in Fig. 5. In the undoped compound we do not see a discontinuity near T_c in the specific heat; there is possibly a small change in slope. Other authors have also observed this curious behavior.[7,8] Some groups have proposed that the zero-field transition in Bi 2:2:1:2 is third order.[1,7] In earlier measurements by us on mixed phase 2:2:1:2-2:2:2:3 unsubstituted samples[9] we did observe two pronounced peaks in C_p/T at the transition temperatures for the 2:2:1:2 and the 2:2:2:3 component; this was also observed in Ref. 8. It is apparent therefore that in the unsubstituted samples this feature is extremely sample dependent. Detailed investigations of the specific-heat anomaly at T_c in BISCO have been published by Braun *et al.*[10] and by Schnelle *et al.*[11] It is found that the character of the anomaly is strongly dependent on oxygen concentration. For samples in the overdoped, oxygen-rich region, the anomaly becomes increasingly indistinct, and the transition temperature drops. From our observed T_c of 77.8 K, we can estimate that the oxygen concentration in our unsubstituted sample $Bi_{1.8}Pb_{0.2}Sr_2CaCuO_y$ is near $y=8.22$. This estimate is also in agreement with the normal-state susceptibility.[12] At $y=8.22$, the specific-heat anomaly is almost absent

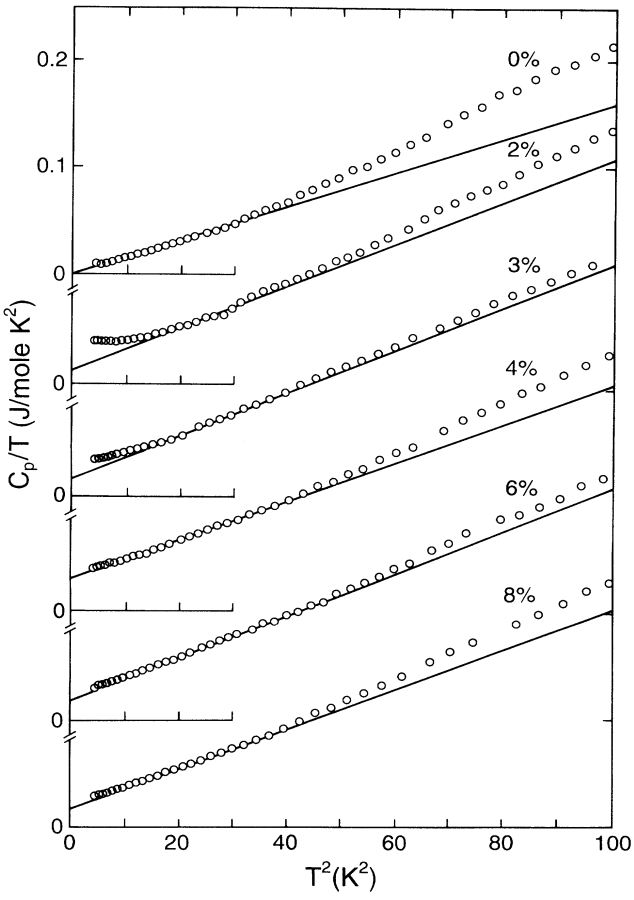

FIG. 4. The specific heat C_p/T as a function of T^2 in the low-temperature range for $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}Co_x)_2O_y$. The lines represent the terms $\gamma_0 T+\beta T^3$ in the fit of Eq. (3). The cobalt concentration is shown in %.

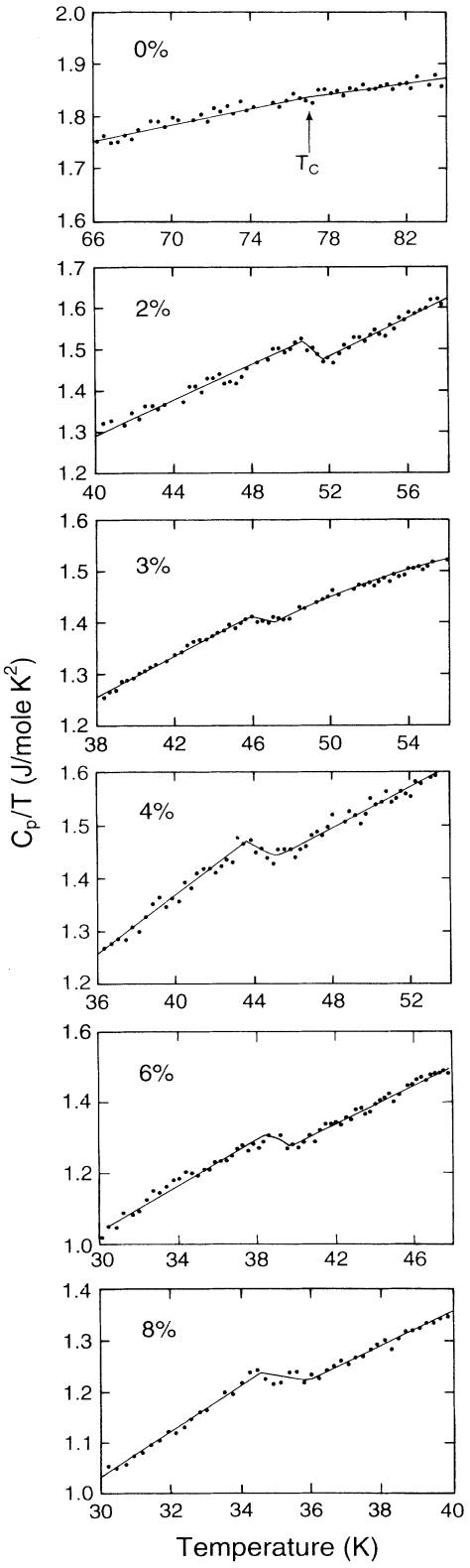

FIG. 5. The specific heat C_p/T as a function of temperature in the transition temperature range for $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}Co_x)_2O_y$. The cobalt concentration is shown in %. For $x=0$, the magnetic transition temperature is shown. The lines are guides to the eye.

according to Ref. 11. It is, however, surprising that Co substitution introduces a distinct anomaly. The reasons for this, and for the absence of an anomaly in all Zn-substituted samples, need further investigation. In Table I we include the discontinuity $\Delta C_p/T_c$ for these transitions, and their transition temperatures, designated T_c. The transition temperatures at T_c agree well with the observed magnetic transition temperatures. It is obvious from the data on the transition at T_c that Co substitution does not change the amount of superconducting phase as judged by the size of $\Delta C_p/T$. This observation is supported by the fact that the observed Meissner fraction is also almost unchanged. Our results show therefore that the linear term in this system is not connected with a reduced amount of superconductivity.

The experimental results can then be summarized as follows. Substitution of Co for Cu in $Bi_{1.8}Pb_{0.2}Sr_2CaCu_2O_y$ introduces a linear term at low temperature into the specific heat. The linear term appears at the lowest Co concentration and apparently saturates at higher Co concentrations. The specific-heat discontinuity at T_c becomes visible. The size of the specific-heat discontinuity, as well as the Meissner fraction show that the amount of superconducting phase has not been reduced with Co substitution. Substitution of Zn for Cu in this compound does not produce any of these phenomena; the specific heat is essentially unchanged from the undoped case. It is interesting that in some samples (2 and 3% Co) a much larger low-temperature term AT^{-2} is observed, although the linear term is smaller than for the larger Co concentrations. In view of these sample differences, therefore, no apparent connection can be made between the low-temperature up-turn and the size of either the linear term or the discontinuity near T_c. This is different from the analysis of the linear term in YBCO by Phillips *et al.*[3] A very definite relation, however, does exist between the normal-state susceptibility and the linear term. This relation is shown in Fig. 6, where both the Curie constant C, and the low-temperature linear term γ_0 are shown as a function of cobalt concentration. The data suggest that there is no minimum cobalt concentration for the appearance of the linear term, although data at still lower cobalt concentration would be desirable.

We believe that the data suggest that the linear term in the Co-substituted samples exists in the superconducting component of the samples, and is introduced by gapless superconductivity[13] as a consequence of the paramagnetic Co impurities. An extensive analysis of the properties of gapless superconductors was given by Skalski, Betbeder, and Weiss[14] and by Maki.[15] These calculations were performed for isotropic, weak-coupling BCS superconductors. It is found that paramagnetic impurities reduce the transition temperature and the specific-heat discontinuity $\Delta C_p/T_c$. Above a certain critical impurity concentration, the energy gap is reduced to zero, while the order parameter is still nonzero. This occurs at the concentration where the transition temperature has been reduced to about 25% of its pure value. The present results indicate the onset of gapless behavior at much smaller paramagnetic impurity concentration, possibly approach-

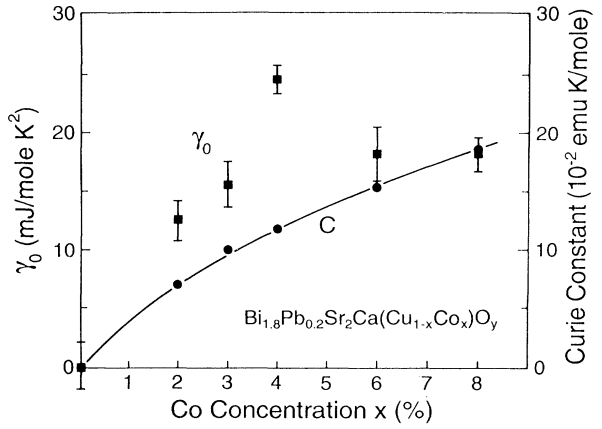

FIG. 6. The linear term of the low-temperature specific heat, γ_0 (squares), and the normal-state Curie constant (dots) for $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}Co_x)_2O_y$ as a function of cobalt concentration.

ing zero concentration. Such behavior would be expected if the gap function is not isotropic, as is to be expected for anisotropic *s*-wave pairing, or *d*-wave pairing. In this case one would expect that paramagnetic impurities would introduce gapless behavior beginning near regions of minimum gap (anisotropic *s* wave) or gap zeros (*d* wave). It is at present not possible to distinguish between gap zeros and very small but finite gaps for highly anisotropic *s*-wave pairing. Evidence for *d*-wave pairing has been accumulating recently, e.g., in the anisotropic NMR relaxation rate[16,17] and the low-temperature penetration depth (in YBCO).[18] In the Bi 2:2:1:2 system there has also been evidence for gapless behavior. Boekholt *et al.*[19] report tunneling measurements on Co-substituted 2:2:1:2 single crystals. They find two gaps, with the smaller one rapidly decreasing with Co concentration. They predict gapless behavior for transition temperatures below about 30 K. Shen *et al.*[20] find from angle-resolved photoemission studies on pure Bi 2:2:1:2 single crystals that the gap function has nodes in agreement with a $d_{x^2-y^2}$ order parameter, and a possible admixture of the gap function has nodes in agreement with a $d_{x^2-y^2}$ order parameter, and a possible admixture of *s*-wave pairing.

The linear term observed in the Co-doped samples is quite large. In all theories of gapless superconductivity it is found that for large paramagnetic impurity concentrations the linear term tends toward the normal-state linear term, see Refs. 13–15 for isotropic *s*-wave pairing, and Ref. 21 for *p*-wave pairing. This is probably the explanation for the limiting value of γ_0 in the range 18–24 mJ/mol K^2 for Co concentrations above about 4%. It is improbable that the limit of γ_0 near 4% Co is due to a solution limit. The paramagnetic susceptibility clearly keeps on increasing beyond this Co concentration and shows no sign suggestive of a solution limit. We believe rather that at this concentration major parts of the gap function have been reduced to zero. The value of γ_0 for the 2:2:1:2 superconductor compares quite well with the value found by Phillips *et al.*[3] for pure $YBa_2Cu_3O_{7-\delta}$, $\gamma_0 = 16$ mJ/mol K^2. Since we believe that both γ_0 and $\Delta C_p/T_c$ originate in the superconducting fraction of our samples, we can estimate then the ratio $\Delta C_p/\gamma_0 T_c$ for $x \geq 4\%$ Co. We find $\Delta C_p/\gamma_0 T_c = 2.23$ (4% Co), 2.95 (6% Co), 3.21 (8% Co). The values are somewhat uncertain due to the large error in $\Delta C_p/T_c$ ($\pm 35\%$), but they point towards moderate strong coupling.

We now turn to the specific-heat discontinuity near T_c. For an isotropic gap function one expects a continuous reduction of $\Delta C_p/T_c$ with paramagnetic impurity content.[14] This effect is, however, smaller than expected; for a reduction of T_c by a factor 2, $\Delta C_p/T_c$ is only reduced to 67% of the pure value. For highly anisotropic *s*-wave or *d*-wave pairing, the reduction of $\Delta C_p/T_c$ could be expected to be even less.[22] One can therefore see that in these cases the specific-heat discontinuity will be only weakly affected by doping (since it depends on the overall gap function), in spite of the appearance of a sizable linear term (which depends primarily on the behavior near the gap zeros).

In conclusion, we find that the substitution of Co for Cu in the Bi 2:2:1:2 superconductor is magnetic, and introduces a linear term in the specific heat at low temperatures. The data are interpreted as gapless superconductivity in a highly anisotropic *s*-wave or *d*-wave superconductor.

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