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Comparison of the low-temperature specific heat of Fe- and Co-doped $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}M_x)_2O_8$ (M=Fe or Co): Anomolously enhanced electronic contribution due to Fe doping

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Specific-heat data of Fe-doped $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}Fe_x)_2O_8$ in the range 2–20 K are presented for $x=1$, 2, 4, 6, and 8 %. The data are compared with our previous measurements on Co-doped bismuth-strontium-calcium-copper oxide superconductors of nominal composition $Bi_2Sr_2CaCu_2O_8$ (BISCO 2212). Both Fe and Co are magnetic substitutions with effective moments close to their free-ion value. In the normal state the magnetic susceptibility increases by more than a factor 2 over the doping range due to effective-mass enhancement. In the superconducting state both ions act as magnetic pair breakers. For Co doping the normal-state linear term γ is observed, enhanced due to the effective-mass increase. For Fe doping we observe a large anomalous contribution to the electronic specific heat starting near 15 K and leading at the lowest temperature to a linear term near $\gamma_0=72$ mJ/mole K^2 (1 mole=1 formula unit). The anomalous term is typical of heavy fermion behavior. Comparison with specific-heat data of Co-doped BISCO 2212 suggests that hybridization between $3d$ electrons of the dopant and the planar carriers is more effective for Fe doping than for Co doping.

In a previous publication,[1] we reported on the low-temperature specific heat of Zn- and Co-doped bismuth-strontium-calcium-copper oxide superconductors of nominal composition $Bi_2Sr_2CaCu_2O_8$ (BISCO). The main result of this work was that Co substitution induces a large linear term in the specific heat, in contrast to Zn substitution, which hardly changes the low-temperature specific heat. From normal-state susceptibility measurements, it was found that Co is a magnetic substitution in BISCO, whereas Zn substitutes nonmagnetically. In the present work, we report our results on the specific heat of Fe-doped BISCO 2212. Fe also substitutes magnetically, and this investigation should therefore be helpful in outlining the relationship between the appearance of a low-temperature linear term in the specific heat of cuprate superconductors and the substitution of magnetic cations. We found again a linear term at low temperatures in Fe-doped BISCO, but this term is much larger than in Co-substituted BISCO. The low-temperature limiting value of γ is at least four times that for Co substitution and much larger than any estimated normal-state linear term. In contrast to this, the normal-state properties of Co- and Fe-substituted BISCO are quite similar. It is possible that hybridization of the Fe wave function with the planar oxygen and copper wave function produces a heavy-fermion-like enhancement of the electronic specific heat, in contrast to the Co case. We will present in this paper the results for Fe-doped BISCO and compare them with the Co-doped BISCO results.

The measurements were conducted on samples of $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}Fe_x)_2O_8$, for $x=1$, 2, 4, 6, and 8 %. The samples were produced by solid-state sintering methods from high-purity Bi_2O_3, PbO, SrO, CaO, CuO, and Fe_2O_3. The oxide mixtures were calcined in air for 24 h at 800 °C and then sintered for a total of 80 h at 845 °C in air. The batches were reground a total of four times in the sintering program. X-ray powder diffraction shows the presence of the 2212 phase, and no indication of the 2223 phase. Small impurity concentrations around 3% were noted.

The superconducting transitions were observed in low fields (1 G) in a superconducting quantum interference device magnetometer. We found that the magnetic transitions have a broad onset and that the transition width increases with increasing Fe concentration or decreasing transition temperature. The transition temperatures given as part of Table III are taken at the 5% level of the field-cooled (Meissner) magnetization (in a field of 1 G). In Fig. 1, we show these transition temperatures as function of Fe concentration as well as the temperature at the 90% level of the Meissner signal.

Investigations of Zn, Fe, and Co doping in the 2212 structure were published by Maeda *et al.*[2] They used a slightly different stoichiometry, $Bi_2(Sr_{0.6}Ca_{0.4})_3(Cu_{1-x}M_x)_2O_y$, and found solution limits of $x=1.5\%$ (M=Zn), $x=8\%$ (M=Fe), and $x=10\%$ (M=Co). We also found a rapid increase in impurity phases when we attempted to exceed $x=8\%$ for either Fe or Co substitution. The decrease in transition temperature T_c in our samples is similar to those found by Maeda *et al.*

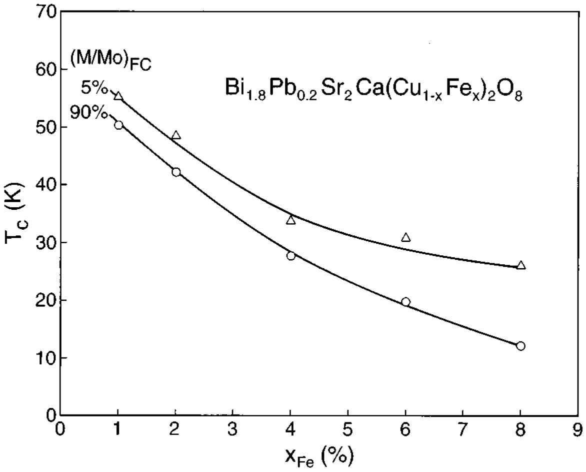

FIG. 1. The temperature T_c at 5 and 90 % of the Meissner signal at 0 K (M_0), measured in a field of 1 G.

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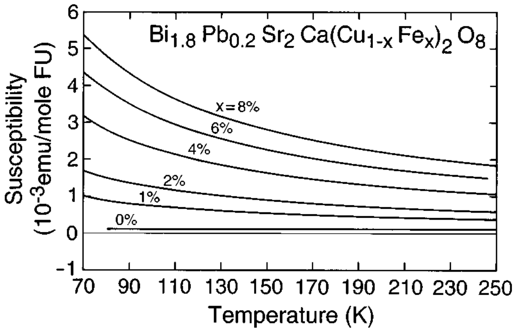

FIG. 2. The normal-state susceptibility of $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}Fe_x)_2O_8$ measured in a field of 5 T.

In Fig. 2 we show the results of our measurements of the normal-state susceptibility as function of temperature for all Fe concentrations; included are also results for an unsubstituted sample. It is obvious that Fe substitution introduces both a Curie term C/T, as well as an enhanced constant term χ_0. We fitted the results therefore to the form

$$\chi=\chi_0+\frac{C}{T}, \tag{1}$$

the resulting values of χ_0 and C are given in Table I. Similar results are given in Table II for Co-substituted samples. We attribute the Curie term C/T (absent in the unsubstituted case) to the magnetic moment of the substituted cation, and interpret the constant term χ_0 as Pauli susceptibility (after correction for diamagnetic core contributions.

The measurements of the normal-state susceptibility χ were confined to the temperature range 70–250 K. The lower temperature is well above the transition temperature T_c for all Fe concentrations. It is, therefore, unlikely that fluctuation effects will affect these data. In Ref. 18, it was found that the fluctuation range in Bi 2212 reaches to about 10% of the transition temperature above T_c (or about 10 K). This puts even the measurements for $x_{Fe}=1\%$ ($T_c=54.8$ K) outside the fluctuation range. As expected, we have not observed any deviation from relation (1) at the low-temperature range for any Fe concentration.

The effective moment p_{eff}, introduced both for Fe and Co substitution was obtained from the measured Curie constant:

$$C=\frac{N(p_{eff}\mu_B)^2}{3k_BT}, \tag{2}$$

where μ_B is the Bohr magneton and N is the molar concentration of Fe or Co. The effective moments are given in Tables I and II and shown in Fig. 3. It can be seen that p_{eff} is slightly concentration dependent, decreasing with increasing solute concentration. In the low concentration limit p_{eff} extrapolates within experimental uncertainty to the moments for the isolated Fe^{2+} ion ($p_{eff}=4.90$), or Co^{2+} ion ($p_{eff}=3.87$), assuming quenching of the orbital moment. The spectroscopic state for Fe would then be $^5D_4$, and for Co, $^4F_{9/2}$. It is clear that the Curie term is directly associated with the solute magnetic moments, and that this moment is very close to the isolated ion value in the limit of infinite dilution. The drop in p_{eff} (which amounts to about 15% for $x=8\%$), can have several reasons. It could be due to spin fluctuations, or a small antiferromagnetic interaction.

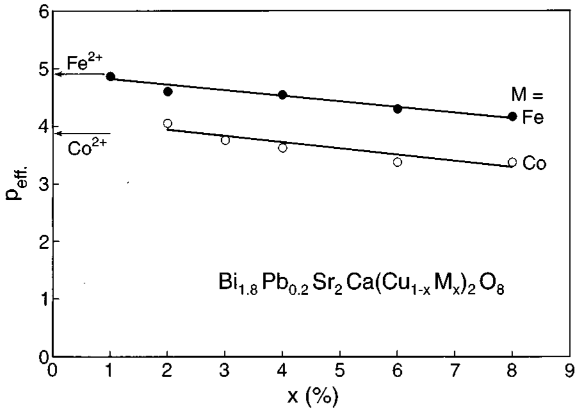

FIG. 3. The effective magnetic moment of Fe and Co in substituted $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}M_x)_2O_8$, $M=$Fe or Co, as function of substitution concentration.

Maeda *et al.*[2] also found a Curie term in their Fe- and Co-substituted samples. They obtained for both cases a p_{eff} of 3.6. This is in quite good agreement with our Co result but distinctly below the p_{eff} we find for Fe substitution, although a slightly larger p_{eff} for Fe substitution is also evident in their results.

In order to discuss the temperature-independent Pauli susceptibility χ_0, we have to correct the data for the diamagnetic core contributions. We estimated these corrections from data given by Gupta[3] from which we estimate the temperature-independent diamagnetic susceptibility as $\chi_{dia}=-2.05\times10^{-4}$ emu/mole, virtually independent of Fe or Co concentration. The "mole" refers here, as in the rest of the paper, to one formula unit, unless reference is specifically made to the Fe or Co content. We neglect the (unknown) van Vleck contribution. For the unsubstituted sample, the susceptibility shows no Curie contribution, and a small constant paramagnetic susceptibility of about 1.0×10^{-4} emu/mole. The corrected susceptibility for this case can then be estimated as

TABLE I. Magnetic properties of the normal state of $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}Fe_x)_2O_8$.

x_{Fe} (%)	C (10^{-3} emu/mole)	p_{eff}	χ_0 (10^{-4} emu/mole)	$\chi_{0,corr}$ (10^{-4} emu/mole)	$\chi_{0,corr}$ (10^{-2} emu/mole Fe)
1	58.57	4.84	1.50	3.55	1.78
2	106.00	4.60	1.86	3.91	0.978
4	207.90	4.56	2.30	4.35	0.544
6	279.30	4.31	3.90	5.95	0.496
8	350.00	4.18	4.70	6.75	0.422

TABLE II. Magnetic properties of the normal state of $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}Co_x)_2O_8$.

x_{Co} (%)	C (10^{-3} emu/mole)	p_{eff}	χ_0 (10^{-4} emu/mole)	$\chi_{0,corr}$ (10^{-4} emu/mole)	$\chi_{0,corr}$ (10^{-2} emu/mole Co)
2	82.6	4.06	1.52	3.57	0.892
3	105.5	3.75	2.18	4.23	0.705
4	131.5	3.62	2.67	4.72	0.590
6	171.5	3.38	3.80	5.85	0.488
8	228.0	3.38	4.20	6.25	0.391

3.05×10^{-4} emu/mole. The interpretation of this constant susceptibility as Pauli susceptibility of free carriers is reasonable. An estimate of χ_{Pauli} from the density of states at the Fermi surface,[4,5] $N(E_F)=3$ states/eV cell, leads to $\chi_{Pauli}=1.94\times10^{-4}$ emu/mole. The observed corrected temperature-independent susceptibility is therefore close to that expected from band-structure calculations. Uncertainties in the diamagnetics corrections, as well as possible uncertainties in the theoretical estimation of $N(E_F)$, may contributed to the observed small difference. We feel in view of this comparison justified in interpreting χ_0 not only in the unsubstituted, but also for the substituted samples as Pauli susceptibility. When Fe or Co are substituted, we observe a large increase of the temperature-independent corrected susceptibility $\chi_{0,corr}$ as shown in Tables I and II and Fig. 4. It is interesting to observe that this increased temperature-independent contribution is, within experimental uncertainty, the same for Fe or Co substitution. At the maximum substitution level of 8% Fe or Co, $\chi_{0,corr}$ has risen to more than twice the value of unsubstituted BISCO. This increase in $\chi_{0,corr}$ is remarkable, and certainly introduced through the magnetic character of the solute, since no such enhancement is observed[1] for the unmagnetic substitution Zn. We will discuss this enhancement further below in connection with the specific-heat results and the Wilson ratio.

The specific-heat data for the Fe-substituted samples are shown in Figs. 5 and 6. In Fig. 5, we show the measured specific heat as function of temperature. In order to obtain the anomalous contribution to C_p in the Fe-doped samples, we subtracted the specific heat of the undoped sample to obtain $\Delta C_p(x)=C_p(x)-C_p(0)$. This contribution is shown in Fig. 6, expressed per mole of Fe substitution. It can be seen that the major effect of Fe substitution is an increased specific heat at low temperatures. The onset of the additional contribution is near 15 K for $x=1$, 2, and 4 % Fe, and somewhat higher temperatures ($\approx$20 K) for $x=6$ and 8% Fe. The extra contribution to C_p rises to a maximum near 7 K and falls off, eventually turning into a temperature-linear term. This behavior is clearly evident from Fig. 6. The temperature-linear term observed at low temperatures is reached near 9 K for 6 and 8 % Fe, near 5 K for 4% Fe, and near 2.5 K for 2% Fe. For the lowest concentration of Fe, $x_{Fe}=1\%$, the linear regime is still not fully established near 2 K. We have in all cases used the estimate given in Fig. 6 by the dotted lines as the low-temperature limit γ_0. It is possible that in the 1% Fe case, a small but not resolved term A/T^2 in the data leads to an overestimate of γ_0 (see analysis below). These low-temperature limiting values γ_0 are given in Table III and Fig. 7. It is apparent that in the Fe-doped BISCO 2212 samples, a very large linear term is observed. The linear term is not very dependent upon Fe concentration, it moves from $\gamma_0=66$ mJ/mole K^2 for $x=1\%$ to $x=73.6$ mJ/mole K^2 for $x=8\%$, but for the higher concentrations, this value is almost independent of x with an average of $\gamma_{0,av}=74.2$ mJ/mole K^2 (averaged for $x=4$, 6, 8%).

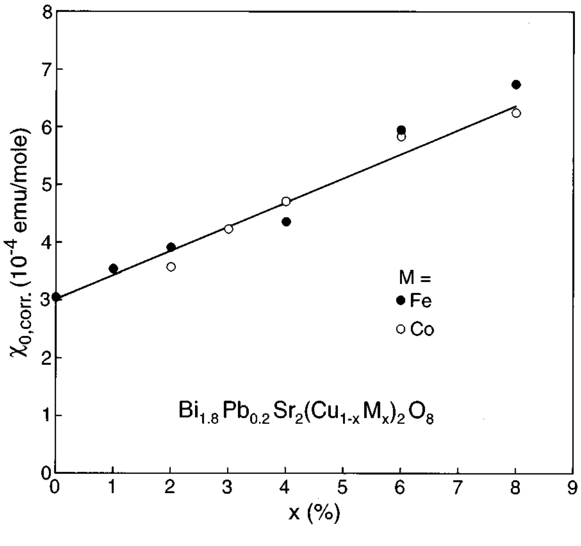

FIG. 4. The corrected temperature-independent susceptibility $\chi_{0,corr}$ from measurements in the normal state in a field of 5 T.

The analysis of the low-temperature specific heat in terms of an anomalously large γ_0 is relatively straightforward for $x_{Fe}=4$, 6, and 8%. For $x_{Fe}=1$ and 2%, however, it is possible that the rise in C_p/T observed at low temperatures may be partially due to the well-known low-temperature upturn observed in many high-temperature superconductors, including Co-doped BISCO.[1] We have, therefore, attempted to fit the specific heat for these two Fe concentrations below 10 K to the form

$$C_p=\frac{A}{T^2}+\gamma_0 T+\beta T^3+mC_E(T), \tag{3}$$

where A/T^2 describes a possible low-temperature system due to Schottky anomalies, βT^3 is the lattice term and $C_E(T)$ an Einstein contribution. For $x_{Fe}=2\%$, we were not able to make such a fit with reasonable parameters, in fact, A turns out to be negative. In the $x_{Fe}=1\%$ case, we can obtain a fit, but with an unreasonably large A ($A=369$ mJ K/mole). This is much larger than values of A typically observed. For Co-doped BISCO, we find that A is typically in the range 20 to 50 mJ K/mole, with one exceptionally large $A=210$ mJ K/mole. Moreover, the fit in the range 2 to 4 K is not good, the

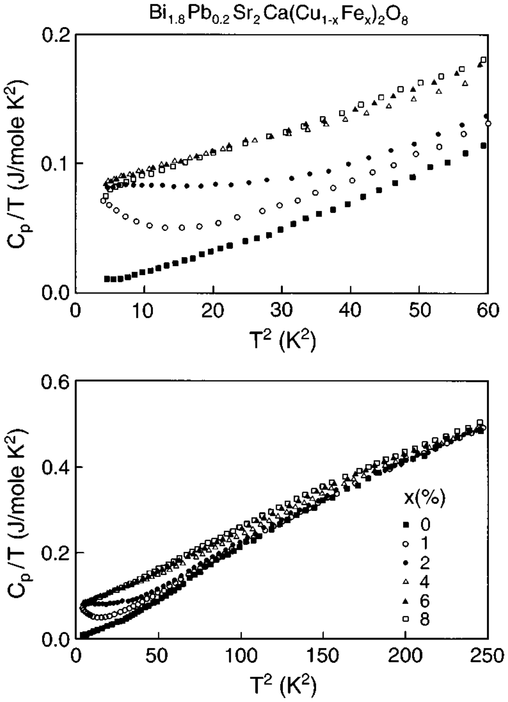

FIG. 5. The specific heat per formula mole of $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}Fe_x)_2O_8$ for different Fe concentrations.

measured C_p/T rises much faster than a term A/T^2 would suggest. It is, therefore, unlikely that the major part of this effect is due to a Schottky-type A/T^2 term. It is, however, possible that a small contribution of this type is present, but its value cannot be reliably estimated.

As can be seen from Fig. 5, any possible linear term in C_p is either absent, or quite small in unsubstituted BISCO, as well as in Zn-doped BISCO.[1] This is in agreement with other work,[6] and makes the detection of substitution-induced linear terms comparatively easy in this system. In recent work[7] on the specific heat of a single crystal of $Bi_2Sr_2CaCu_2O_8$, a small γ near 2.1 mJ/mole K^2 was obtained from analysis in the range 1.5–4.5 K. This term could possibly arise from CuO_2 plane disorder; it is, however, still an order of magnitude below the enhancement found in both Fe- and Co-substituted BISCO.

We have also estimated the entropy content of the anomalous specific-heat contribution. It was obtained by numerically integrating

$$\Delta S=\int_0^{T_{\max}}\frac{\Delta C_p}{T}\,dT, \qquad (4)$$

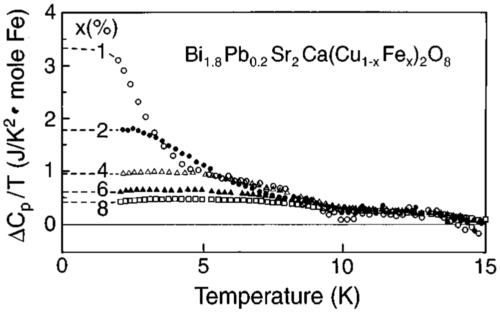

FIG. 6. The difference in specific heat between Fe-substituted and unsubstituted $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}Fe_x)_2O_8$. The data are given per mole Fe.

where $\Delta C_p=C_p(x_{\mathrm{Fe}})-C_p(0)$, and the upper limit is the onset temperature $T_{\max}$ of the anomalous contribution near 15 K. The low-temperature contribution, below about 2 K, is calculated by assuming a linear behavior to the lowest temperatures, as indicated in Fig. 6. The results are given in Table III. We find that the entropy content per mole Fe is strongly concentration dependent. If one expresses ΔS as $\Delta S=R\ln(2S+1)$, then we find in the limit of low concentrations, that S falls between $S=2$ and $S=3$, as shown in Fig. 8. A more accurate determination is not possible due to the large contributions from the extrapolated regions below 2 K. The rather large value of ΔS found for $x=1\%$ Fe is more uncertain than those for the higher Fe concentrations due to the large required extrapolation to $T=0$ (about 35%), as well as uncertainties in the exact level of Fe concentration. The range of possible S values in the limit of low concentration is, however, certainly in agreement with the $^5D_4$ state suggested by the normal-state susceptibility.

Comparison of the present system with Fe-doped pure Cu, suggests that the spectroscopic state of Fe is different in that system. In $\underline{\mathrm{Cu}}$-Fe one also finds an additional specific-heat term,[8,9] its entropy content has been obtained by Triplett and Phillips[9] as $\Delta S=R\ln 4$, giving $S=3/2$. This spin value is also in agreement with the susceptibility of $\underline{\mathrm{Cu}}$-Fe measured by Hurd[10] ($p_{\mathrm{eff}}=3.68$) and by Tholence and Tournier[11] ($p_{\mathrm{eff}}=3.4$). It appears, therefore, that Fe substitutes in BISCO in a higher spin state, than in pure copper and that this state is closer to the free-ion value. The large dependence of ΔS on Fe concentration shows that complete disorder of Fe spins at high temperatures is obtained only at quite low concentrations, somewhat below 2%.

The temperature-independent term of the specific heat and the Pauli susceptibility in metallic systems can be compared

TABLE III. Parameters of the anomalous specific-heat contribution in $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}Fe_x)_2O_8$.

x_{Fe} %	T_c (K)	γ_0 (mJ/mole K^2)	γ_0 (mJ/mole Fe K^2)	Normalized Wilson ratio	ΔS (J/mole Fe K)	S ($\Delta S=R\ln(2S+1)$)
1	54.8	66.0	3300	0.392	16.1	2.96
2	48.5	70.4	1760	0.404	11.9	1.59
4	33.8	73.6	920	0.431	8.6	0.90
6	30.9	75.6	630	0.573	6.4	0.58
8	26.1	73.6	460	0.668	4.9	0.40

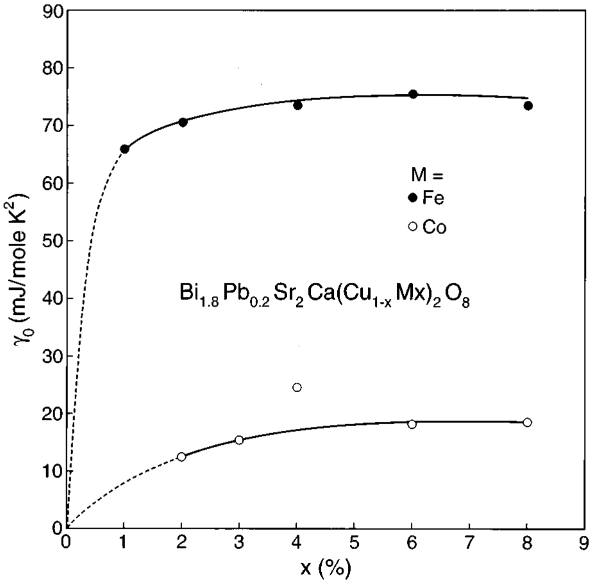

FIG. 7. The low-temperature limiting linear term in the specific heat of Fe- and Co-substituted $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}M_x)_2O_8$, M=Fe,Co. Data are given per formula mole.

by using the Wilson ratio defined as $R=\chi_0/\gamma_0$. In here both χ_0 and γ_0 are to be taken in the low-temperature limit. For an ideal Fermi system, one has

$$R_{\text{ideal}}=\frac{3}{\pi^2}\left(\frac{\mu_B}{k_B}\right)^2, \tag{5}$$

where μ_B is the Bohr magneton. Experimentally obtained Wilson ratios are usually reported in reduced form, $R_{\text{norm}}=R/R_{\text{ideal}}$. In the present case we take γ_0 as the low-temperature limiting value of γ, but χ_0 has to be obtained from measurements above T_c. Wilson ratios obtained in this way are given in Tables III and IV and shown in Fig. 9. For Co-substituted BISCO we have a normalized Wilson ratio very close to 2 (with the exception of the 4% Co case, where we found a somewhat larger γ). As was shown earlier (Fig. 4), χ_{corr} changes between about 3×10^{-4} emu/mole to about 6.5×10^{-4} emu/mole over the range 0–8 % of Co or Fe substitution, i.e., more than a factor 2. In spite of this, the Wilson ratio for Co substitution remains near 2. This shows that the enhancement of $\chi_{0,\text{corr}}$ and of γ_0 in this case are probably due to the same cause. It was shown by Maeda *et al.*[2] that Co or Fe doping of BISCO 2212 leave the carrier concentration almost unchanged (doping independent Hall coefficient). It is therefore likely that this enhancement is due to an increase in effective mass, approximately by a factor 2 for the substitution range 0–8 %, for these two systems. Co- and Fe-doped BISCO is therefore in some respect similar to the incipient Mott insulator $Sr_{1-x}La_xTiO_3$ investigated by Tokura and co-workers.[12,13] These authors find that in their system the metal-insulator transition is characterized by a critical effective-mass enhancement, but a constant carrier density. These authors also find a Wilson ratio near $R_{\text{norm}}=2$ and analyze it in terms of Fermi-liquid theory. Here

$$R_{\text{norm}}=(1+F_0^a)^{-1}, \tag{6}$$

where F_0^a is one of the Landau parameters describing the Fermi liquid. A Wilson ratio of $R_{\text{norm}}=2$ gives $F_0^a=-0.5$, and this value is approximately independent of doping level.

TABLE IV. Linear specific-heat term and Wilson ratio of $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}Co_x)_2O_8$.

x_{Co} (%)	T_c (K)	γ_0 (mJ/mole K^2)	γ_0 (mJ/mole Co K^2)	Normalized Wilson ratio
2	50.7	12.6	315	2.06
3	48.6	15.6	260	1.97
4	43.0	24.7	309	1.39
6	38.8	18.3	152	2.33
8	35.8	18.4	115	2.47

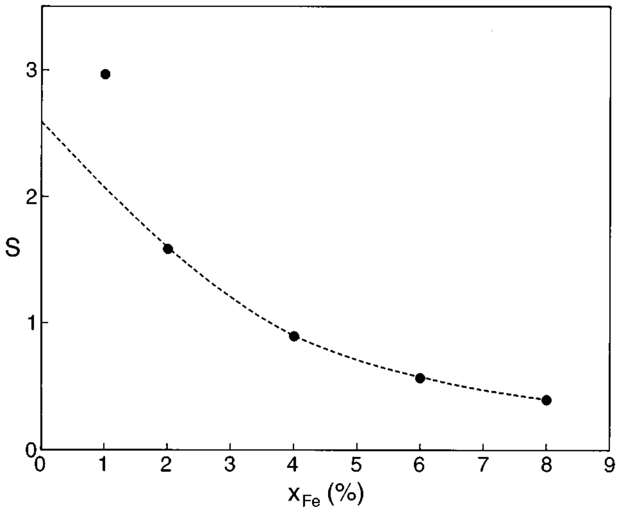

FIG. 8. The effective spin S obtained from the entropy content ΔS of the anomalous specific-heat contribution per mole of Fe substitution of $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}Fe_x)_2O_8$. ΔS is given by $\Delta S = R\ \ln(2S+1)$.

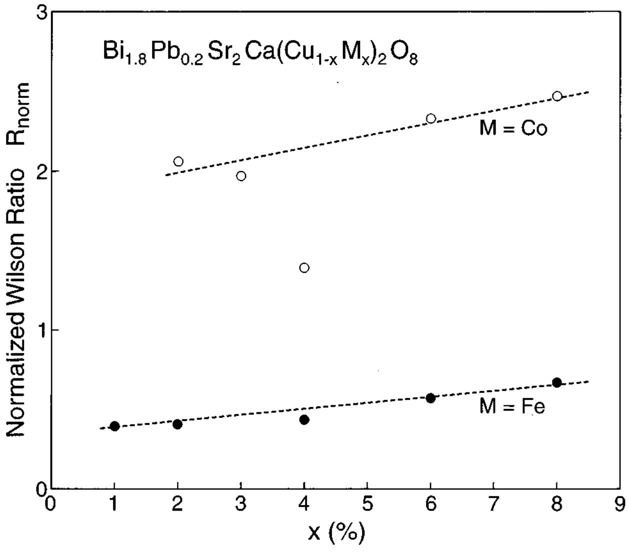

FIG. 9. The Wilson ratio of Fe- and Co-substituted $Bi_{1.8}Pb_{0.2}Sr_2Ca(Cu_{1-x}M_x)_2O_8$, M=Fe,Co.

The slight increase in R_{norm} seen in Fig. 9 is probably still within experimental uncertainty. For $R_{\mathrm{norm}}=2.5$, which is close to the Wilson ratio for $x=8\%$, we find $F_0^a=-0.6$, this should define the range of possible values of F_0^a.

A value of $R_{\mathrm{norm}}=2$ is also predicted for $S=1/2$ Kondo systems.[14,15] Reviews of R_{norm} for intermetallic systems have also been given,[16,17] values close to 1 or slightly larger are usually found.

Our interpretation of the data for Co-doped BISCO is then that the normal-state Pauli susceptibility is enhanced due to effective-mass enhancement. Magnetic pair breaking in the superconducting state introduces a linear specific heat term γ which is essentially the normal state γ and which shows the same effective-mass enhancement with Co doping. For the undoped case we have $\chi_{0,\mathrm{corr}}=3.05\times10^{-4}$ emu/mole. Using a Wilson ratio of $R_{\mathrm{norm}}=2$ for this case, we would estimate a γ_0 of 11 mJ/mole K^2 for unsubstituted BISCO 2212. This γ_0 cannot be directly observed due to the opening of the gap but it can be estimated from other data. For this we can, e.g., use the observed anomaly in C_p at T_c. A detailed analysis of this was given by Braun *et al.*,[18] who analyzed a variety of observed ΔC_p in BISCO 2212 in terms of fluctuation contributions and a "BCS" linear term γ in C_p, assumed to extend to T_c. They find values of γ_{BCS} between 2.8 and 10.9 mJ/mole K^2. These estimates are based on the ideal BCS ratio $\Delta C_p/(\gamma_{\mathrm{BCS}}T_c)=1.43$. Since ΔC is the fitted parameter, a ratio larger than 1.43 would decrease the "experimental" γ_{BCS}. In spite of the difficulties of estimating the correct γ_0 for the undoped case, it is likely that R_{norm} close to 2 holds also for this case.

For Fe-doped BISCO we find in the normal state similar behavior to the Co-doped system. The increase in $\chi_{0,\mathrm{corr}}$ with doping is the same as for Co doping and we interpret this again as due to an approximate twofold increase in effective mass over the doping range. The low-temperature behavior is, however, quite different. Here the normalized Wilson ratio varies between 0.39 and 0.67, with an average value of 0.49. This much smaller Wilson ratio is entirely due to the approximately fourfold increase in the low-temperature limiting term of γ compared to Co-doped BISCO. These large values are anomalous and cannot be explained simply by the recovery of the normal-state density by doping due to gapless behavior. One should, of course, also use the limiting low-temperature value of the susceptibility for calculations of the Wilson ratio. This is not possible since χ_{normal} cannot be obtained in the superconducting state. We therefore can also not extrapolate the Wilson ratio in this case to the undoped limited. We have, therefore, only the specific-heat data as indicators of anomalous behavior at low temperatures.

Since the large increase in γ_0 is related to the magnetic Fe substitution, it is also instructive to present the effect in terms of the molar Fe content. This is done in Table III and shown in Fig. 10. As one can see, the low-temperature limiting term γ_0 in terms of Fe content is enormous, and reminiscent of heavy fermion behavior. In fact for the 1% Fe BISCO sample, the linear specific-heat term per magnetic ion is only exceeded by that found[19] in CePt$_2$Sr$_2$ ($\gamma_0=10\,000$ mJ/g atom K^2). Another similarity between these results and heavy fermion systems is the temperature dependence of the linear term, as shown in Fig. 6.

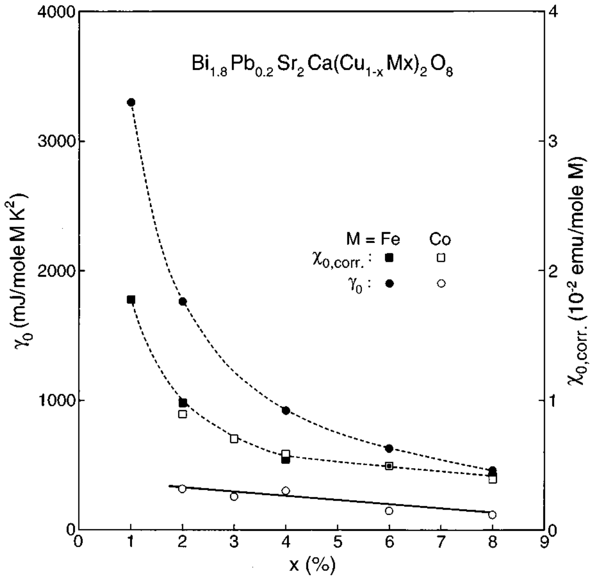

FIG. 10. The low-temperature limiting linear term γ_0 of the specific heat and the corrected temperature-independent susceptibility, $\chi_{0,\mathrm{corr}}$ of Fe- and Co-substituted Bi$_{1.8}$Pb$_{0.2}$Sr$_2$Ca(Cu$_{1-x}M_x$)$_2$O$_8$, M=Fe or Co. Data are given per mole of magnetic substitution.

The main result of this work is the large enhancement of the specific heat below about 15 K in Fe-doped BISCO, leading at low temperatures to a large linear term. This linear term is much larger than can be reasonably expected from the normal-state properties and it is also much larger than the linear term found in Co-doped BISCO. Similar large enhancements of the specific heat have been found previously in two other doped cuprate superconductors, (Y$_{1-x}$Pr$_x$)Ba$_2$Cu$_3$O$_{7-\delta}$ (Refs. 20–23) and (Y$_{1-x}$Tb$_x$)Ba$_2$Cu$_3$O$_7$.[24] Maple *et al.*[20] and Jin *et al.*[23] analyzed their data in terms of a Kondo anomaly. Phillips and co-workers[21,22] describe the anomalous contribution in the Pr-doped Y-Ba-Cu-O as heavy fermion like. For a concentration of 30% Pr they find an onset of the anomaly near 50 K and a low-temperature linear term γ_0 of 200 mJ/mole Pr K^2, or 63 mJ/mole K^2 (1 mole=1 formula unit). Cao *et al.*[24] find (by fitting in the range 4–10 K) a γ of 180 mJ/mole Tb K^2 or 58 mJ/mole K^2 for Tb-doped Y-Ba-Cu-O with 37% Tb. These results are quite similar to those reported here for Fe-doped BISCO. In both of the doped Y-Ba-Cu-O system it is assumed that the $4f$ electrons hybridize with the mobile carriers, leading to heavy fermion behavior similar to other heavy fermion systems. The difference between these results and ours is that we have a $3d$ substitution and that the enhancement of γ per mole of magnetic substitution is much larger. Hybridization between $3d$ electrons and the planar carriers in BISCO is therefore much stronger. It is, however, not clear whether the normalization to magnetic ion content is the best way of looking at the data. It is indeed remarkable that the enhanced γ per formula unit (and therefore also per CuO$_2$ plane) is remarkably similar in all three systems (63 mJ/mole K^2 in Pr-doped Y-Ba-Cu-O, 58 mJ/mole K^2 in Tb-doped Y-Ba-Cu-O and about 72 mJ/mole K^2 in Fe-doped BISCO). Since we have two planes per formula unit in each of these systems, we find an enhanced γ of about 30 to 35 mJ/Cu plane K^2 in all of these systems. A reason for this similar behavior is not known.

A second important result arises from the comparison between Co-and Fe-doped BISCO. The Co results can, as has been shown, be understood as due to magnetic pair breaking and recovery of the normal state γ. This normal state γ is enhanced due to an increase in effective mass similar to the mass enhancement found in the normal state from $\chi_{0,\mathrm{corr}}$. For Fe-doped BISCO a very large additional enhancement of γ_0 is observed which is similar to heavy fermion systems. A possible explanation of this difference may lie in the different wave function of Fe and Co substitution. As we have shown, the normal-state susceptibility makes it likely that Fe substitutes in a D state and Co in a F state. If this symmetry is maintained in the octahedral crystal environment, then the Fe wave function will more readily hybridize with the oxygen orbitals than the Co wave function. We are at present not aware of any other possibility of explaining the difference between Fe and Co substitution.

The main picture that evolves then is that the magnetic substitutions Co and Fe in BISCO 2212 increase the effective mass of carriers in the normal state by approximately a factor of 2 over the doping range 0 to 8%. The magnetic ions act as pair breakers. The linear specific heat in the Co-doped systems is close to the expected normal-state linear term with the same effective-mass enhancement. For Fe-doped BISCO pair breaking again produces a linear specific heat at low temperatures but this term is anomalously enhanced and heavy fermion like. The difference in behavior may be due to the different magnetic state in which Co and Fe substitute in BISCO 2212.

It is interesting to note in this context that only magnetic substitutions produce this effect in BISCO. The substitution of Zn, which is unmagnetic in BISCO, does not introduce gaplessness (at least it does not introduce a linear term in the specific heat). We believe that this result is not expected in d-wave scenarios of high-T_c superconductivity where both magnetic and nonmagnetic substitutions should have similar effects.

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