PHYSICAL REVIEW B VOLUME 53, NUMBER 5 1 FEBRUARY 1996-I

Effect of substituting Ce at the Ca site on the high-temperature superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$

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(Received 3 February 1995)

We have investigated the system $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+\delta}$ $(0 \leqslant x \leqslant 0.5)$ to study the effect of substituting Ce for Ca on superconductivity in the $Bi_2Sr_2CaCu_2O_{8+\delta}$ system (T_c=90 K). It is observed that, on 25 at. % substitution of Ce for Ca, superconductivity is completely suppressed. This is relatively faster suppression of superconductivity compared to that seen on substituting other rare earths for Ca where ~50 at. % substitution is required to suppress superconductivity. Magnetic susceptibility of the $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+\delta}$ compounds is found to be weakly temperature dependent showing a small rise at low temperatures and a shallow minima at about 200 K. These results suggest the possible existence of Ce in a tetravalent state rather than in a trivalent state in this system. X-ray-diffraction studies on these compounds indicate a decrease in the *c* lattice parameter with increased substitution of Ce. This is consistent with nearly tetravalent Ce ion replacing the Ca^{2+} ion since the size of Ce^{3+} is comparable to that of Ca^{2+}, while that of Ce^{4+} is smaller.

I. INTRODUCTION

In many high-T_c superconducting families of compounds, the rare earths (R) play a vital role in establishing the proper structure. The magnetic interaction of the rare-earth ions with electrons/holes responsible for superconductivity is generally found to be very weak in these oxide systems so that superconductivity is not affected by the presence of magnetic rare-earth ions which otherwise act as pair breakers in many systems. In so far as rare-earth-based $RBa_2Cu_3O_{7-y}$ (R:123) compounds are concerned, Ce, Pr, and Tb compounds present an interesting situation as they do not show superconductivity, unlike other rare-earth-based R:123 compounds.[1,2] A great deal of work has been done on $R_{1-x}Pr_xBa_2Cu_3O_{7-y}$ compounds (see, for instance, Refs. 3–5). The depression of superconducting transition temperature T_c in these compounds with increasing Pr concentration has been explained in more than one way, such as hole filling mechanism based on the tetravalent state of Pr,[3,4] by localization of mobile holes[6] considering the rare earths to be in the trivalent state and also by the pair-breaking effect due to the magnetic $4f$ electrons of Pr which are presumed to hybridize with the conduction electrons/holes.[7,8] The case of Ce and Tb is even more interesting since these do not even substitute isostructurally in the R:123 lattice.

In the $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi:2212) system, there have been several studies on the cationic substitution of Ca by the rare earths (see, for instance, Refs. 9–11). Complete replacement of Ca by rare earths can be achieved which results in the suppression of T_c. However, in this regard, reports on the Ce, Pr, and Tb doping are very few.[12–14] Recently, we have examined, in detail, the effect of Pr and Tb substitution at the Ca site on the superconductivity in $Bi_2Sr_2CaCu_2O_{8+\delta}$.[15] In this paper we present the results of Ce substitution in $Bi_2Sr_2CaCu_2O_{8+\delta}$. We find that Ce can be substituted up to 50 at. % at the Ca site in $Bi_2Sr_2CaCu_2O_{8+\delta}$. Superconductivity is completely suppressed in this system at about 25 at. % Ce substitution. Magnetic-susceptibility and x-ray-diffraction studies suggest that Ce ions are largely in a tetravalent state in these compounds.

II. EXPERIMENTAL DETAILS

Samples of $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+\delta}$ with x=0.0, 0.1, 0.2, 0.25, 0.3, 0.4, and 0.5 were synthesized from the solid-state reaction route. Details of the heat treatment are given elsewhere.[13] The samples were examined by x rays at room temperatures using a JEOL x-ray diffractometer to determine their phase purity and the lattice parameters. Low-field (50 Oe) susceptibility measurements were made using a superconducting quantum interference device magnetometer to look for the superconducting transition through the onset of diamagnetic signals. Standard four-probe dc resistivity measurements were also carried out on these samples to confirm the superconducting transition temperature (T_c) values. High-field (5 kOe) paramagnetic susceptibility measurements were made in the normal state of the samples in the temperature range of 2–400 K to obtain information about the magnetic moment and the nature of Ce ions.

III. RESULTS AND DISCUSSION

Powder x-ray-diffraction studies on the above-mentioned Ce-substituted Bi:2212 samples suggest that these are single phase in nature. The observed lines can be indexed on the basis of an orthorhombic structure. The lattice parameters, obtained from a least-squares fit of the observed d values, are given in Table I. The a lattice parameter of $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+\delta}$ system increases, while the c lattice parameter decreases with increasing Ce substitution. An increase in the a lattice parameter is due to the excess oxygen in the system accompanying the replacement of Ca^{2+} by Ce, which is consistent with similar replacement of Ca^{2+} by other R^{3+} ions.[10,11] The c lattice parameter of these samples is found to decrease with increasing Ce substitution for Ca in this system.

Results of low-field susceptibility measurements on $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+\delta}$ samples are shown in Fig. 1, where susceptibility is plotted as a function of temperature. It is noted that while $Bi_2Sr_2CaCu_2O_{8+\delta}$ is superconducting with diamagnetic onset superconducting T_c of 95 K, the T_c

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TABLE I. Lattice parameters *a*, *b*, and *c* (with error bar of ±0.0008 Å), and superconducting transition temperature T_c (dia) for $Bi_2Ca_{1-x}Ce_xSr_2Cu_2O_{8+\delta}$. NSC stands for samples not superconducting down to 5 K.

x	*a* (Å)	*b* (Å)	*c* (Å)	T_c (dia) (K)
0.0	5.4023	5.4271	30.8037	95
0.10	5.4059	5.4273	30.7145	52
0.20	5.4145	5.4267	30.6491	25
0.25	5.4217	5.4215	30.5238	NSC
0.30	5.4235	5.4234	30.4657	NSC
0.40	5.4289	5.4317	30.4035	NSC
0.50	5.4319	5.4329	30.3749	NSC

decreases with increasing Ce concentration. Four-probe dc resistivity measurements confirm the T_c values obtained from low-field susceptibility measurements. The T_c values for various superconducting samples of the $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+\delta}$ series are given in Table I and are also plotted in Fig. 2 as a function of Ce concentration *x*. Complete suppression of superconductivity is observed for $x \geqslant 0.25$. This implies that even 25 at. % Ce substitution for Ca is sufficient to quench superconductivity in the Bi:2122 system, while for other rare earths, the corresponding concentration is above 50 at. %.[9–11]

It is interesting to mention here that Ce can exist in a material in 3+ or in 4+ or in an intermediate valence state; the trivalent state being the most commonly observed. The ionic size of Ce^{4+} is smaller than that of Ca^{2+}, while that of Ce^{3+} is comparable to that of Ca^{2+} in the same coordination number.[13] Since the *c* parameter of the $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+\delta}$ system is seen to decrease with substitution of Ce for Ca, crystallographically it seems that Ce exists more towards its 4+ valence state in this system. As remarked above, replacement of Ca by Ce quenches superconductivity of Bi:2122 much faster in comparison with other rare earths. Because the T_c depression in Bi:2122 due to rare-earth substitution does not depend on the rare-earth ion magnetic moment,[9–11] the other possibility in such a situation is the effect of hole filling due to alliovalent substitution. Therefore, the present results suggest that the hole filling due to the substitution of nearly tetravalent Ce for divalent Ca is more than that in the case of other trivalent rare earths which can happen if Ce exists in 4+ valence state in this system.

To substantiate the above reasoning, we have carried out magnetic-susceptibility measurements on $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+\delta}$ samples in the paramagnetic state. It is worth mentioning here that Ce^{3+} $(4f^1, {}^6F_{5/2})$ is a magnetic ion which gives rise to a Curie-Weiss-type temperature-dependent susceptibility, while Ce^{4+} $(4f^0)$ ion is completely nonmagnetic and gives rise to largely temperature-independent susceptibility. Figure 3 shows a plot of susceptibility versus temperature for various $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+\delta}$ samples in a field of 5 kOe. It is observed that the susceptibility of all the samples is small and largely temperature independent, especially above 100 K, with a shallow minimum around 200 K, indicating that the Ce ions are in the nonmagnetic state. At low temperatures (below 100 K) there is a small Curie-Weiss tail in the susceptibility which suggests the presence of a small fraction of Ce^{3+} ions often stabilized by lattice defects, impurities or local variations in the oxygen content.

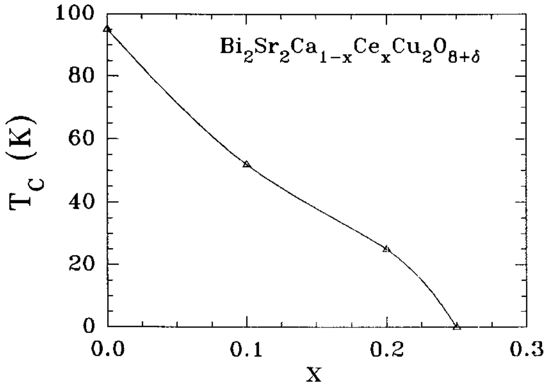

FIG. 2. T_c versus *x* behavior for the $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+\delta}$ system.

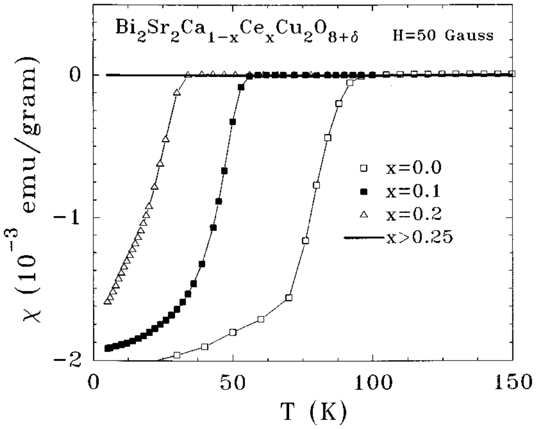

FIG. 1. Low-field magnetic susceptibility vs temperature for the $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+\delta}$ system for various values of *x*. Samples with $x \geqslant 0.25$ are nonsuperconducting.

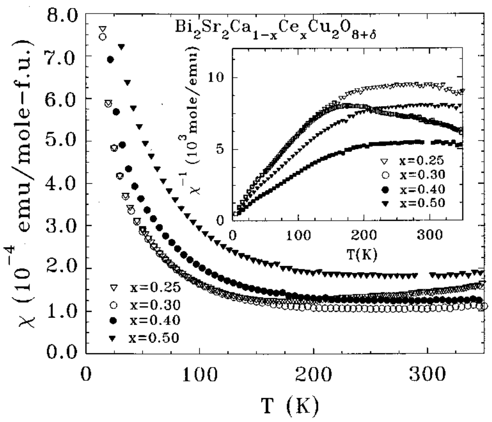

FIG. 3. Plot of magnetic susceptibility vs temperature for the $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+\delta}$ system for different *x*. Inset shows the plot of inverse susceptibility vs temperature for the same samples.

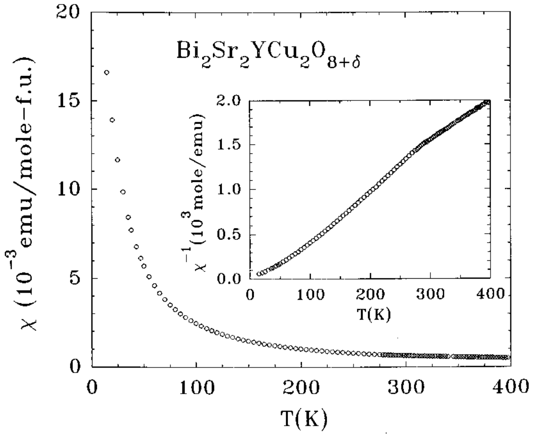

FIG. 4. Plot of magnetic susceptibility vs temperature for $Bi_2Sr_2YCu_2O_{8+\delta}$. Inset shows the plot of inverse susceptibility vs temperature for the same.

It is interesting to compare the magnetic behavior of the $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+\delta}$ system (Fig. 3) with that of the $Bi_2Sr_2YCu_2O_{8+\delta}$ system (Fig. 4). Both Y^{3+} and Ce^{4+} are nonmagnetic ions. Hence the observed susceptibility of these systems in a clean phase is supposed to contain the possible contribution of copper moments only. It is noteworthy that, in the case of the Y-substituted Bi:2212 sample, the magnetic susceptibility is two orders of magnitude higher than that of the Ce-substituted samples. In fact the Cu moments are presumed to order antiferromagnetically in the Y-substituted sample at high temperatures ($T_N \sim 300$ K).[11] In both the situations, superconductivity is not observed down to a temperature of 5 K. Nonobservation of superconductivity in these compounds is thought to be due to the decrease in the number of carriers (holes) in Cu-O planes. As both Y and Ce reside between the two flat Cu-O planes in Bi:2212 structure, it appears that Ce^{4+} has an influence on the adjacent Cu-O planes resulting in a lowering or quenching of the Cu moments as well.

As far as the effect of rare-earth substitution for Ca on the superconductivity of $Bi_2Sr_2CaCu_2O_{8+\delta}$ is concerned, the entire rare-earth family can be divided as follows. First are those rare earths which possess the 3+ valence state in these compounds, e.g., Y, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Tm, etc.;[9–11] and the second are the nearly tetravalent ones, e.g., Ce. Depending on their formal valence states in doped $Bi_2Sr_2CaCu_2O_{8+\delta}$ system, different rare-earth ions substituted at the Ca^{2+} site neutralize holes from the adjacent Cu-O planes and, as a result, completely suppress superconductivity of the system at a critical concentration of the doped rare earth whichdepends on the rare-earth valence. This critical concentration is about 50 at. % for trivalent rare-earth ions. In the present situation of Ce^{4+} doping, the hole filling is twice as large as in the case of trivalent rare-earth ions and, therefore, only about 25 at. % Ce is sufficient to quench the superconductivity of the $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+\delta}$ system.The suppression of T_c by Pr falls in between these two categories since about 40 at. % Pr is sufficient to completely suppress superconductivity in the Bi:2212 system. This coupled with the fact that the Pr effective moment is intermediate between that of Pr^{3+} and Pr^{4+} may suggest hybridization of the Pr $4f$ states with conduction electrons/holes in Bi:2212 system. However, this needs to be investigated further.

IV. SUMMARY AND CONCLUSIONS

The above results can be summarized as follows:

(1) Up to 50 at. % substitution of Ca by Ce, single phase $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+\delta}$ materials are formed with a monotonically decreasing c lattice parameter.
(2) In comparison with other trivalent rare earths, the amount of Ce required for quenching superconductivity of the Bi:2212 system is nearly half (~25%).
(3) Magnetic-susceptibility measurements reveal that Ce is nonmagnetic in the $Bi_2Sr_2Ca_{1-x}Ce_xCu_2O_{8+\delta}$ system implying a valence state of nearly 4+ for Ce.

In conclusion, x-ray diffraction, low- and high-field magnetic-susceptibility results indicate that Ce exists in the nearly 4+ state in the Bi:2212 system. As a result, it provides comparatively more hole filling in the system than other rare earths and leads to relatively faster quenching of superconductivity.

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