Low-dimensional magnetic ordering and Ising- and XY-like anisotropy of Er^{3+} in the system $ErBa_2Cu_3O_x$ with $6 < x < 7$

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Magnetic ordering of Er^{3+} ions in $ErBa_2Cu_3O_x$ with $6.12 \leq x \leq 6.91$ has been studied for both orthorhombic and tetragonal phases by means of magnetic-susceptibility and heat-capacity measurements. Superconductivity in the orthorhombic phase samples was confirmed by the onset of a diamagnetic susceptibility. The superconducting transition temperature T_c was observed to decrease from 92 to 55 K as x was reduced from 6.91 to 6.31. The tetragonal samples with $x=6.23$ and 6.12 remained paramagnetic down to 1.2 K and showed no overt trace of diamagnetism. The states of Er^{3+} ions in $ErBa_2Cu_3O_6$ and $ErBa_2Cu_3O_7$ were calculated by means of crystalline electric field (CEF) theory using both a point-charge model and scaled inelastic neutron scattering results for $HoBa_2Cu_3O_7$. The calculated susceptibility is in excellent agreement with data on the tetragonal specimens for 1.2 K $\leq T \leq$ 160 K. For the orthorhombic samples, sharp heat-capacity peaks which resemble those for a two-dimensional Ising system and evidently correspond to the magnetic ordering of Er^{3+} moments are found. The transition temperature T_m decreases smoothly from 0.604 to 0.545 K as x is varied from 6.91 to 6.31. In contrast, tetragonal samples show only a broad rounded heat-capacity anomaly having its maximum at 0.5 K and closely resembling that for a one-dimensional XY model. The change of Er^{3+} ion anisotropy from Ising-like to XY-like is explained by the CEF calculation which shows the ground state to be planar for the tetragonal phase but with the b axis slightly favored in the orthorhombic structure. Randomness in the coupling of Er^{3+} moments caused by structural disorder may effectively reduce the dimensionality of magnetic ordering as has been found in the case of random dilution. These results imply that the dominant magnetic interactions of Er^{3+} ions in these materials are of short range.

INTRODUCTION

Following the discovery of superconductivity below $T_c \approx 92$ K in $YBa_2Cu_3O_7$,[1] it was quickly established that Y^{3+} ions in this compound can be fully replaced by most trivalent rare-earth ions without significantly affecting T_c or the superconducting behavior.[2-5] More recently, it has been found that the magnetic moments of the R^{3+} ions order antiferromagnetically at low temperatures $T_m \ll T_c$ for $R \equiv$ Nd, Sm, Gd, Dy, and Er.[6-12] Typically $T_m \approx 1$ K or less, the largest value, $T_m = 2.2$ K, occurring for $R \equiv$ Gd. The mechanism of the weak interionic coupling responsible for this ordering has been the subject of considerable discussion. T_m is small enough to suggest that dipolar interaction is important and perhaps dominant. Any exchange interaction present would presumably be indirect, involving electrons belonging to the copper-oxygen sheets lying above and below the widely separated layers of R^{3+} ions. The insensitivity of T_c to the choice of R^{3+} suggests that these ions interact negligibly with the electrons responsible for the superconductivity which apparently reside on the same two-dimensional copper-oxygen arrays. Were these the only electrons available to mediate an indirect exchange coupling of R^{3+}'s, it would appear that such exchange was negligible and dipolar coupling, indeed, dominant.

However, two recent theoretical developments indicate that such a conclusion may not be justified. Buzdin and Bulaevski[13] cite the behavior of the small-angle diffuse magnetic scattering of neutrons from $ErBa_2Cu_3O_7$ as strong evidence for a Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction among R^{3+} moments in such systems and show how this could occur via the electrons responsible for their superconductivity. At the same time, Liu[14] has shown that R^{3+} moments in $RBa_3Cu_3O_7$ may interact via conduction electrons virtually occupying states more than ~ 1 eV above (or below) the Fermi level. This leads to a modified RKKY-type coupling of R^{3+} moments and ordering independent of the superconductivity of the material.

Several additional observations also suggest that such nondipolar R^{3+} interactions may be important in the $RBa_2Cu_3O_7$ compounds. For example, the antiferromagnetic alignment of R^{3+} moments along the c direction seen in $GdBa_2Cu_3O_7$ below T_m (Ref. 15) seems unlikely with pure dipolar coupling. Two-dimensional Ising-like

behavior found near T_m for many members of the series[9,10,16] suggests that the dominant interactions are short range and thus nondipolar. In those cases where ordering is observed, T_m is found[9-12] to scale roughly as the de Gennes factor, $(g_J-1)^2J(J+1)$, in spite of the fact that crystal-field splitting of the lowest J multiplet is significant for some R^{3+} ions in these materials.

The $R\mathrm{Ba_2Cu_3O_x}$ compounds with $6 \lesssim x \lesssim 7$ can be obtained in closely related orthorhombic and tetragonal structures depending on oxygen content and the oxygen microstructure.[17,18] The high-T_c (≈ 92 K) orthorhombic phase occurs for $x \simeq 7$. Reducing x yields orthorhombic superconductors with lower T_c's and, eventually ($x \lesssim 6.3$) nonsuperconducting tetragonal semiconductors. Several groups have shown that T_m and the C_p anomaly associated with ordering in orthorhombic $\mathrm{GdBa_2Cu_3O_7}$ are only slightly altered by the removal of oxygen and conversion to the tetragonal form.[19-22] The Gd^{3+} lattice is essentially the same in the two structures. These facts are consistent with the assumption that nondipolar R^{3+} interactions are negligible in $R\mathrm{Ba_2Cu_3O_x}$ compounds and are among the strongest items of evidence for that view. It should be noted, however, that many estimates of T_m using only dipolar coupling give values that are much too small.[9,16] At the same time, recent neutron diffraction data on $\mathrm{GdBa_2CuO_x}$ below T_m give different ordered spin configurations for orthorhombic and tetragonal phases,[23] a fact which is very difficult to explain with dipolar interaction alone. Perhaps the most direct indication of the presence of nondipolar interaction between Gd^{3+} ions in $\mathrm{GdBa_2Cu_3O_x}$, however, is provided by the observation[24] of exchange narrowing of the paramagnetic resonance signal. The coupling constant J/k_B is found to be 0.1 K corresponding to an exchange field at room temperature $H_{ex}=5300$ Oe. This is significantly larger than the estimated dipole field $H_{dip} \approx 3000$ Oe.

While superconductivity in the $R\mathrm{Ba_2Cu_3O_x}$ compounds is strongly dependent on structure and oxygen content, the evidence for $\mathrm{GdBa_2Cu_3O_x}$ suggests that rare-earth magnetic ordering is in many ways independent of those factors. However, the Gd^{3+} ion, with its $L=0$ ground state, is a rather special case. We consider it a matter of fundamental interest to examine the effects of structure and oxygen content on the magnetic ordering of other R^{3+} ions in $R\mathrm{Ba_2Cu_3O_x}$ compounds. In addition to providing perhaps further insight into the mechanism of interaction between R^{3+} ions, such studies should reveal effects characteristic of the interaction of the single R^{3+} ion with its crystalline environment. For example, the difference in symmetry of the crystalline electric field in the orthorhombic and tetragonal structures can have a significant effect on the nature of the ground states (single-ion anisotropies) of certain rare-earth ions. It has been shown that the moment of the Er^{3+} ion ($L=6$, $S=\frac{3}{2}$) has a preference for orientation in the a-b plane.[25,26] In this case, a change from tetragonal to orthorhombic symmetry could have a profound effect on the magnetic anisotropy and ordering. To explore such questions, we have measured heat capacities and magnetic susceptibilities of powder samples of $\mathrm{ErBa_2Cu_3O_x}$ as a function of x and crystal class at temperatures down to 0.1 K. We have also performed crystal-field calculations to obtain estimates of the nature and degree of single-ion anisotropy in these materials.

EXPERIMENTAL DETAILS

Samples of $\mathrm{ErBa_2Cu_3O_{6.91}}$ were prepared by solid-state reactions of appropriate amounts of $\mathrm{Ba(NO_3)_2}$, $\mathrm{Er_2O_3}$, and CuO. The reaction mixture was heated to 700 °C in order to decompose the $\mathrm{Ba(NO_3)_2}$ to BaO. After regrinding, samples were heated in air to 950 °C for 24 h, then annealed at 450 °C for 24 h in a flowing O_2 atmosphere. $\mathrm{ErBa_2Cu_3O_{6.91}}$ prepared in this way was orthorhombic and single phase as determined by powder x-ray diffraction. The oxygen stoichiometry of 6.91 was determined by iodometric titration with an accuracy of ± 0.03.[27]

Samples of $\mathrm{ErBa_2Cu_3O_x}$ were prepared by annealing $\mathrm{ErBa_2Cu_3O_{6.91}}$ at appropriate temperatures in a flowing N_2 atmosphere. In all cases the oxygen stoichiometry was determined by iodometric titration. Except for the two nominally tetragonal specimens with $x=6.15$ and $x=6.34$, x-ray diffraction evidence of a single phase was unambiguous. The diffraction spectra in these two cases [see Fig. 1(b)] resemble very closely those reported for the tetragonal phase [see Fig. 1(c)] in peak position and relative intensity. However, they reveal very small splittings of what in the tetragonal case should be the (200) and (020) reflections. These findings led us to prepare samples with $x=6.12$ and $x=6.23$ for which the x-ray powder diffraction patterns proved free of this complication and

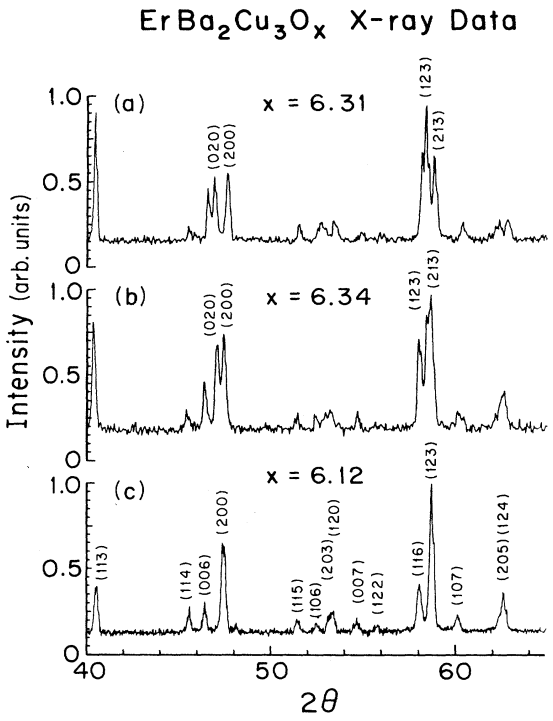

FIG. 1. Powder x-ray diffraction patterns for $\mathrm{ErBa_2Cu_3O_x}$ samples: (a) $x=6.31$, (b) $x=6.34$, (c) $x=6.12$. For (a) and (b), splitting of the (200) and (020) reflections and thus their orthorhombicity is evident.

TABLE I. Preparative conditions for $ErBa_2Cu_3O_x$. Values of x have an accuracy of ± 0.03.

x	Symmetry	Reaction conditions in flowing N_2
6.12	tetragonal	550 °C×20 h + 600 °C×8 h
6.23	tetragonal	430 °C×16 h + 600 °C×4 h
6.15	tetragonal?	550 °C×24 h
6.34	tetragonal?	540 °C×5 h
6.31	orthorhombic	425 °C×16 h
6.67	orthorhombic	410 °C×16 h

tetragonal symmetry was clearly established [see Fig. 1(c)]. The reaction conditions for all samples are listed in Table I.

In addition to the x-ray diffraction data taken at the time of sample preparation, additional powder spectra were obtained on portions of the sample material used in calorimetric and magnetic measurements immediately before and after they had been subjected to the handling and thermal cycling necessary in that work. The diffraction patterns showed no appreciable change for a given sample. Some of the results for orthorhombic and tetragonal samples are shown in Fig. 1 and tabulated in Table II. The lattice constants inferred from these data agree well with values reported in the literature.[4,17]

Heat capacities were measured between 0.4 and 100 K by a discontinuous heating method using a ^{3}He-cooled, fully automated vacuum calorimeter. C_p determinations were extended down to ~0.1 K by a similar technique in a ^{3}He-^{4}He dilution refrigerator. Details of these procedures have been reported elsewhere.[28] We have measured the magnetic susceptibilities of all samples between ~1.2 and 160 K by an ac mutual inductance method at a frequency of 80 Hz with a field amplitude of approximately 3 Oe. Pressed pellet and packed powder samples gave essentially the same results after correction for the demagnetizing effect of the shielding current.

RESULTS AND DISCUSSION

A. Magnetic susceptibility

The magnetic susceptibilities of powder samples of all of the $ErBa_2Cu_3O_x$ compounds studied in this work are plotted as functions of the temperature over the interval ~1.2 to 160 K in Fig. 2. Above ~90 K, χ_p is very nearly the same for all samples and is dominated by a contribution of the Curie-Weiss form $C/(T-\Theta)$. The observed Curie constant in this region, $C \approx 10.9$ K cm^3/mole, is essentially that for the free Er^{3+} ion in its $^4I_{15/2}$ ground state. Evidently the crystalline electric field acting on these ions is weak although the averaging inherent in the powder measurement may tend to obscure rather significant splittings of the ground J multiplet. It is seen in Figs. 2 and 3 that the tetragonal specimens with $x=6.12$ and 6.23 remain paramagnetic with χ_p increasing as T falls to its lowest value. The data depart from the high-temperature Curie-Weiss law below ~70 K in a way which reflects the crystal-field splitting of the free ion ground state. Below ~10 K, χ_p follows a new Curie-Weiss law with an added temperature-independent term α. Assuming only a lowest Kramers doublet with an effective spin $S'=\frac{1}{2}$ to be populated at these temperatures, the new Curie constant $C=4.8$ K cm^3/mole yields an average splitting factor $g_{ave}=7.2$. This agrees well with the average of $g_\parallel$ and $g_\perp$ measured for the ground doublet of Er^{3+} in several other structures with axially symmetric crystal fields.[29] The fitted Weiss constant in this region, $\Theta=-0.5$ K, is antiferromagnetic in sign and much closer in magnitude to the magnetic ordering temperature of the orthorhombic material, $T_m \leq 0.6$ K, than the Weiss constant one obtains from data taken above 90 K, namely, $\Theta=-10$ K. Crystal-field splittings dominate interionic interactions in the latter case.

We have calculated the crystalline electric field (CEF) effect on Er^{3+} ions explicitly using the Stevens operator equivalent method.[30] The CEF parameters obtained for $HoBa_2Cu_3O_7$ by inelastic neutron diffraction measurements[31,32] were scaled for the case of Er^{3+} ions. We also calculated the CEF parameters with a point-charge model which assigns $+3e$ to Er, $+2e$, to Ba, $-2e$ to O, and the charge balance to Cu. Although such a calculation did

TABLE II. Lattice constants of $ErBa_2Cu_3O_x$ specimens.

x	a (Å)	b (Å)	c (Å)
6.12	3.836	· · ·	11.733
6.23	3.850	· · ·	11.772
6.15	3.839	3.868	11.762
6.34	3.836	3.864	11.754
6.31	3.822	3.876	11.713
6.67	3.812	3.890	11.670
6.91	3.814	3.887	11.661

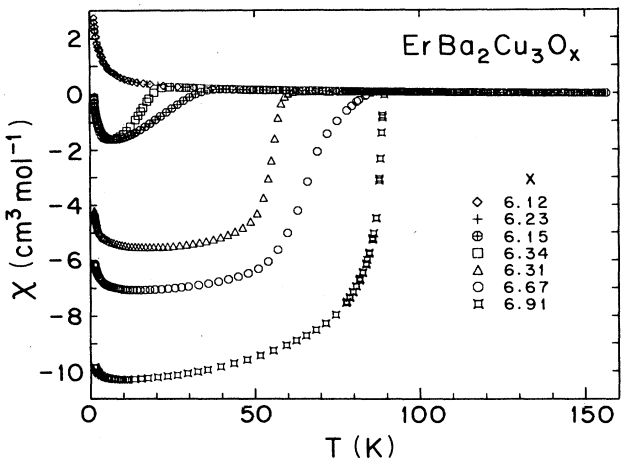

FIG. 2. Magnetic susceptibilities of powder samples of $ErBa_2Cu_3O_x$ as functions of temperature. Onset of diamagnetism caused by a superconducting phase transition is seen except for the tetragonal samples with $x=6.12$ and 6.23.

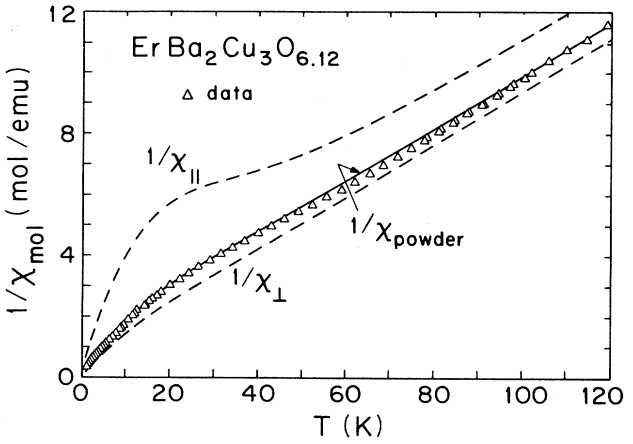

FIG. 3. Inverse susceptibility of the tetragonal $ErBa_2Cu_3O_{6.12}$ sample as a function of temperature. Theoretical curves are shown for the applied field parallel and perpendicular to the c axis (dashed lines) as well as for the powder samples (solid curve).

not yield quantitative agreement with experimental susceptibility results, the overall features of the CEF splitting were reproduced.[26] We used the results of those calculations for $ErBa_2Cu_3O_7$ and $ErBa_2Cu_3O_6$ to obtain the ratios of the CEF parameters and thus to convert the extrapolated parameters for $ErBa_2Cu_3O_7$ to those for $ErBa_2Cu_3O_6$. Both sets of parameters are presented in Table IV together with the calculated energy levels of the Er^{3+} ion. The magnetic susceptibilities were calculated by direct numerical diagonalization of a spin Hamiltonian matrix which includes the Zeeman term. The results for $ErBa_2Cu_3O_6$ are compared with the experimental data for $x=6.12$ in Fig. 3. The agreement is excellent especially with the consideration that no adjustable parameters are involved in these calculations.

In Fig. 2 we see that χ_p becomes negative at sufficiently low temperatures for all samples except those with $x=6.12$ and $x=6.23$ whose tetragonal character is well established. In the case of the fully oxygenated orthorhombic sample ($x=6.91$), the onset of superconductivity occurs at $T_c \approx 90$ K. Initially, the fall of χ_p is rather abrupt below that point suggesting that the specimen is quite homogeneous. Eventually χ_p reaches a minimum value which corresponds to $\sim 85\%$ of the sample volume being superconducting and ideally diamagnetic. Reduction in the oxygen content lowers T_c for a given sample while raising the minimum value of its χ_p. It appears that the creation of additional oxygen vacancies reduces the fraction of sample volume contributing to the diamagnetism and, presumably, to the superconductivity.

While these results are in general agreement with those of Takabatake *et al.*[17] they include an added feature, namely, an upturn in χ_p at low temperatures where the Er^{3+} paramagnetism becomes appreciable. At the lowest temperatures, the curves for $x=6.91$, 6.67, and 6.31 as well as $x=6.34$ and 6.15 can be fitted with a Curie-Weiss law plus a negative constant term χ_0. The fitted Curie constant increases as both x and the constant term decrease in magnitude. Such behavior appears to be consistent with a decrease in the shielding of Er^{3+} moments by super currents as the fraction of the specimen volume which is superconducting is reduced. In Fig. 4, the χ_0 term is plotted against the Curie constant C for all the $ErBa_2Cu_3O_x$ samples studied. All the data points lie on a straight line which gives $C_0=4.84$ K cm^3/mole for $\chi_0=0$ and $\chi_\infty=-13.5$ cm^3/mole for $C=0$. This might be taken to suggest that these packed powder specimens comprise superconducting and nonsuperconducting regions and that these two parts respond to external fields almost independently. In fact, the extrapolated Curie constant, $C_0=4.84$ K cm^3/mole for $\chi_0=0$ is very close to the value $C=4.80$ K cm^3/mole obtained for the $x=6.12$ sample which does not show any sign of superconductivity. When the sample consists solely of superconducting material one would expect that $\chi_0=-V_{\rm mol}/4\pi(1-D)$ where $V_{\rm mol}$ is the molar volume of $ErBa_2Cu_3O_x$ and D is the demagnetizing factor. Assuming that $D=\frac{1}{3}$ and $V_{\rm mol}=104$ cm^3/mole, one obtains $\chi_0 \simeq -12.4$ cm^3/mole. This agrees well with the extrapolated value χ_∞. The paramagnetic contribution estimated from the magnitude of the Curie constant and the diamagnetic contribution from that of the χ_0 value are tabulated in Table III. In each case, these two percentages add up almost exactly to 100%. It is not clear to what microscopic entities these superconducting and nonsuperconducting regions correspond. As discussed in the previous section, the x-ray diffraction peaks of all our samples are quite sharp and reflection index assignments are unambiguous. It is not likely that these samples are simply mixtures of two distinct phases, one, for example, orthorhombic with $x \simeq 7$, the other tetragonal with $x \simeq 6$, so that the local stoichiometry would be quite different from the average value of x measured chemically on the bulk materials. On the other hand, given the limited resolution of the x-ray study, one cannot rule out the possibility that some of our samples are mixtures of superconducting and nonsuperconducting phases with almost matching

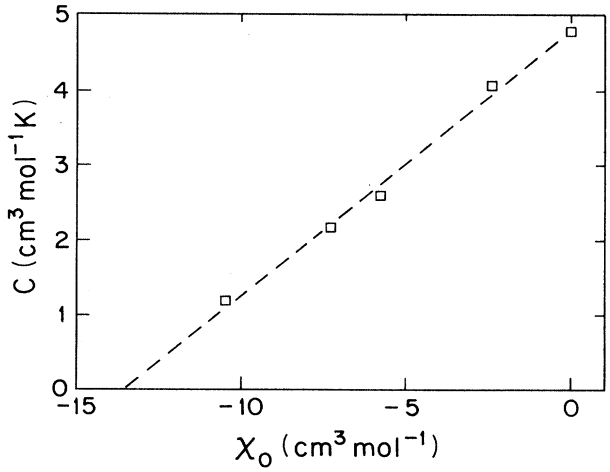

FIG. 4. The Curie constant C determined by a Curie-Weiss fit to the susceptibility upturn in $ErBa_2Cu_3O_x$ samples in the superconducting state is plotted against the diamagnetic susceptibility χ_0 as described in the text.

TABLE III. Diamagnetic and paramagnetic contributions in the $ErBa_2Cu_3O_x$ system. $C_0=4.83$ K cm^3/mole, $\chi_\infty=-13.5$ cm^3/mole. For definitions, see text.

x	Symmetry	T_c (K)	C (K cm^3/mole)	(a) $C/C_0\times100$ (%)	χ_0 (cm^3/mole)	(b) $\chi_0/\chi_\infty\times100$ (%)	(a)+(b) (%)
6.12	tetragonal	· · ·	4.80	99	· · ·	0	99
6.23	tetragonal	· · ·	4.80	99	· · ·	0	99
6.15	tetragonal?	35	4.08	84	−2.42	18	102
6.34	tetragonal?	20	4.08	84	−2.42	18	102
6.31	orthorhombic	55	2.61	54	−5.78	43	97
6.67	orthorhombic	85	2.18	44	−7.28	54	98
6.91	orthorhombic	92	1.198	25	−10.46	77	102

lattice constants. However, as discussed below, there is a dramatic change in the low-temperature magnetic heat capacity associated with the ordering of Er^{3+} moments which corresponds to rather abrupt change in lattice constants. Furthermore, the onset of a diamagnetic susceptibility occurs at lower temperatures and remains sharp as x decreases. This is difficult to explain with the mixed-phase model alone. We believe that our samples are essentially single-phase material and that the variation of the ratios of the superconducting to nonsuperconducting volume reflects the change in the penetration of external fields as the value of x changes.

B. Heat capacity

The magnetic contribution to the heat capacity is shown in Fig. 5 for the $x=6.12$ (tetragonal) and $x=6.91$ (orthorhombic) samples. The correction for the lattice contribution was estimated from the data[9] for $YBa_2Cu_3O_7$. Unlike the Gd or Dy systems,[19,33] there is a striking difference between the heat capacities of tetragonal and orthorhombic samples of $ErBa_2Cu_3O_x$. While the $x=6.91$ sample exhibits a sharp cooperative heat-capacity peak at 0.60 K, only a broad rounded heat-capacity anomaly is seen for the $x=6.12$ specimen. One difference with our previous measurements for an $x\cong7$ sample[9] is that the conspicuous broad anomaly originally found at 5 K is no longer in evidence. Similar anomalies have been reported independently by several groups[7,34] all of which apparently used similar techniques, including $BaCO_3$ as a starting material, in sample preparation. It is possible that these procedures promoted the development of a common impurity phase in all of these specimens. However, we found no obvious indication of the presence of such a phase in our sample by x-ray diffraction. At the same time, the 5-K anomaly rather clearly contained the spin entropy of a significant fraction of the Er^{3+} ions in the sample and these did not seem to be involved in the two-dimensional ordering of the others. In fact, the case was made[9] that they appeared to be coupled in linear chains. Comparison of the original data with those for our new $x=6.91$ sample suggests that, while the 5-K anomaly has been suppressed, at least part of its entropy is still present in the form of enhancement of the higher-temperature side of the 0.60-K C_p peak seen in Fig. 5. It is possible that different preparative procedures might lead to different kinds of distribution of oxygen vacancies in these materials and thus produce samples in which R^{3+} ions were coupled predominantly in two-dimensional (2D) sheets or in some mixture of one- and two-dimensional arrays.

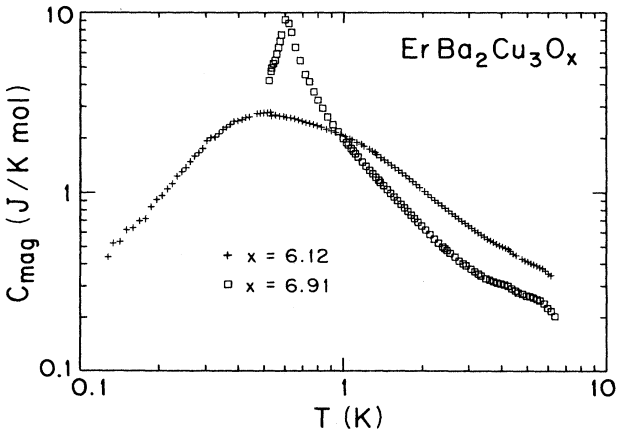

FIG. 5. Magnetic heat capacities of $ErBa_2Cu_3O_x$ with $x=6.91$ (orthorhombic) and $x=6.12$ (tetragonal) as functions of temperature below 8 K.

Additional heat-capacity data were taken for samples with varied oxygen content x. The results below 2 K are shown in Fig. 6. For orthorhombic samples with $x=6.91$, 6.67, and 6.31, sharp heat-capacity peaks which mark the onset of long-range magnetic ordering are found. As was the case with our earlier results for an orthorhombic specimen,[9] each of these peaks strongly resembles that expected for a 2D Ising magnet. The transition temperature T_m decreases gradually as x decreases. On the other hand, nominally tetragonal samples (with or without any trace of orthorhombicity) do not show any sharp anomalies for $x=6.12\sim6.34$. The magnetic transition temperature T_m is plotted against x in Fig. 7. For the orthorhombic specimens, it is possible to extend the $C_p(T)$ curve from the lowest measured point ($T\simeq0.5$ K) to $T=0$ K using a

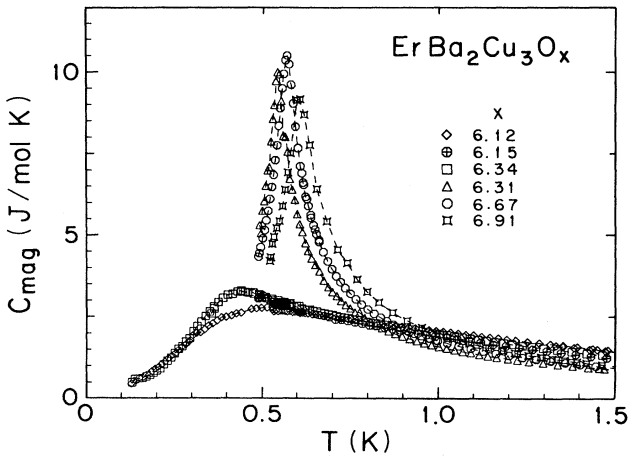

FIG. 6. Magnetic heat capacities of $ErBa_2Cu_3O_x$ specimens with $6.12 \leq x \leq 6.91$ between 0 and 1.5 K. Curves shown are merely guides to the eye.

suitably scaled 2D Ising C_p function and to evaluate the entropy $S(T) = \int_0^T C_p d\ln T$. The entropies of all of these samples reach a plateau at $R\ln 2$ between about 10 and 20 K. The entropy change involved in the extrapolation of the data amounts to $\sim 20\%$ of $R\ln 2$. The extrapolation to 0 K of data on the tetragonal samples is much less uncertain. The calculated entropy again exhibits a plateau at $R\ln 2$ between ~ 5 and 15 K. The contributions of the ground doublets of all Er^{3+} ions are thus accounted for over roughly the same temperature range in each of the $ErBa_2Cu_3O_x$ compounds studied.

We have already seen that the CEF theory gives a good account of the susceptibility data for the $x=6.12$ and $x=6.23$ samples. The same calculation predicts that the first excited doublet state of Er^{3+} lies about 119 K above the ground doublet for $x=7$ and at about 96 K for $x=6$ (see Table IV). Schottky-like anomalies were observed near 45 K for both the $x=6.91$ and $x=6.12$ samples. These evidently correspond to the thermal population of this and still higher doublets. The calculated ground-state moments are tabulated in Table IV. For $x=7$, the anisotropy is strongly planar with the b axis slightly favored. We believe that the essentially 2D Ising-like behavior of the $x=6.91$ system arises from the anisotropy within the a-b plane. The gradual decline in T_m for the orthorhombic samples may be due at least in part to the decrease in that anisotropy as the oxygen content x decreases. At the same time, of course, T_c is changing (see Fig. 2) and with it, presumably, characteristics of the electrons in the copper-oxygen sheets with which it seems likely that the Er^{3+} ions interact, if only weakly. It is possible, therefore, that the lowering of T_m with x may also reflect a reduction in the indirect exchange interaction between Er^{3+} ions as well as the reduction of the in-plane anisotropy. These two effects may be intimately linked.

When x is further reduced below ~ 6.3, $RBa_2Cu_3O_x$ becomes tetragonal, the anisotropy in the a-b plane disappears and the Er^{3+} ionic moments should behave like XY spins. It seems reasonable from structural considerations to suppose that the XY interaction would couple these spins in two-dimensional arrays and to try to interpret the heat-capacity data on that basis. Monte Carlo calculations[35] reported for the 2D, $S=\frac{1}{2}$ XY model display a rounded heat-capacity anomaly (not unlike the one we observe,) near the temperature of the unusual transition expected in such systems. The calculated curve for $J/k = 0.45$ K is shown in Fig. 8 together with the experimental data for the tetragonal $x=6.12$ sample. The agreement is rather poor. However, also shown in Fig. 8 is a theoretical curve for a one-dimensional $S=\frac{1}{2}$ XY model obtained with the exact results of Katsura[36] assuming $J/k = 0.83$ K. The agreement with experiment is striking over a relatively large range of temperature. It should be noted that the value of C_{mag} at the maximum of this curve is not adjustable. Contrary to simple expectation, this coupled quantum XY system is better described by a 1D than a 2D model. Evidently, Er^{3+} spins in tetragonal $ErBa_2Cu_3O_x$ do not undergo a phase transition and exhib-

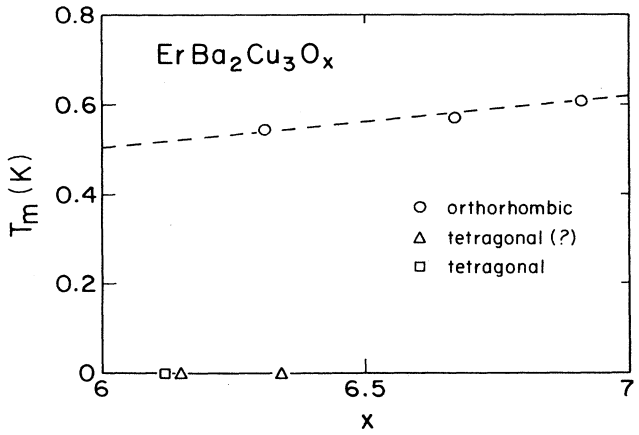

FIG. 7. Magnetic ordering temperature T_m of Er^{3+} moments in $ErBa_2Cu_3O_x$ as a function of x.

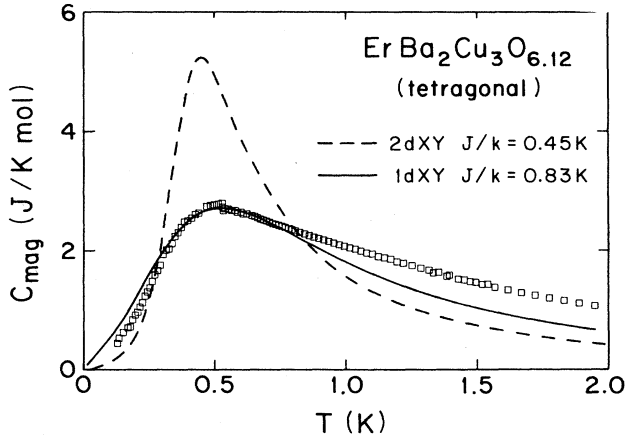

FIG. 8. Magnetic heat capacity of tetragonal $ErBa_2Cu_3O_{6.12}$ between 0 and 2 K. Theoretical curves are shown for two $S=\frac{1}{2}$ XY antiferromagnets: (a) 2D, $J/k = 0.45$ K (dashed curve); (b) 1D, $J/k = 0.83$ K (solid curve).

TABLE IV. Crystalline electric field parameters, ground-state moments, and energy levels for Er^{3+} in $ErBa_2Cu_3O_x$. The B_n^m are coefficients in the expansion of the CEF Hamiltonian in equivalent operators O_n^m, i.e., $H_{cryst}=\sum B_n^m O_n^m$. All tabulated energy levels are Kramers doublets. Inelastic neutron scattering (INS) data on $HoBa_2Cu_3O_7$ are from Refs. 31 and 32. For details of point-charge model (PCM) see text.

	Er:O_6	Er:O_7	Ho:O_7	Er:O_6	Er:O_7
B_n^m (K)	(scaled from Ho INS data)			(from PCM)	
B_2^0	3.28×10^{-1}	5.97×10^{-1}	-5.45×10^{-1}	1.81	3.30
B_2^2	0.00	2.29×10^{-1}	-2.09×10^{-1}	0.00	7.71×10^{-1}
B_4^0	-1.44×10^{-2}	-1.35×10^{-2}	1.10×10^{-2}	-6.48×10^{-3}	-6.07×10^{-3}
B_4^2	0.00	8.56×10^{-4}	-6.96×10^{-4}	0.00	1.82×10^{-3}
B_4^4	5.54×10^{-2}	5.99×10^{-2}	-4.87×10^{-2}	3.24×10^{-2}	3.50×10^{-2}
B_6^0	7.53×10^{-5}	7.38×10^{-5}	-5.22×10^{-5}	9.24×10^{-6}	9.06×10^{-6}
B_6^2	0.00	-5.42×10^{-5}	3.83×10^{-5}	0.00	-3.41×10^{-6}
B_6^4	2.11×10^{-3}	2.22×10^{-3}	-1.57×10^{-3}	3.48×10^{-4}	3.65×10^{-7}
B_6^6	0.00	-2.46×10^{-5}	1.74×10^{-5}	0.00	1.41×10^{-7}
		Ground-state moments (μ_B)			
μ_a	3.95	3.92		5.59	3.13
μ_b	3.95	4.09		5.59	7.13
μ_c	2.06	1.89		0.635	0.469
		Energy levels (K)			
E_0	0	0		0	0
E_1	96	119		33	49
E_2	124	147		115	150
E_3	144	149		195	262
E_4	672	682		307	389
E_5	695	727		336	488
E_6	747	783		363	555
E_7	786	826		374	579

it only short-range magnetic ordering above ~0.1 K. To the extent that interactions among these 1D XY chains are negligible, this situation could persist down to $T=0$.

We have found that still further improvement of the fit of the experimental heat-capacity data on the tetragonal $ErBa_2Cu_3O_x$ specimens is possible if it is assumed that Er^{3+} ions in these materials are actually divided into two independent magnetic subsystems having 1D XY and 2D XY character, respectively. As shown in Fig. 9, surprisingly good agreement with the experimental data can be obtained with such models by a proper choice of the three adjustable parameters, namely, the interaction constants J_{1D} for the 1D and J_{2D} for the 2D XY spin systems and a fraction of 1D systems r. Figure 9 displays the results for the tetragonal specimen with $x=6.12$ as well as for the $x=6.34$ sample which is nominally tetragonal but exhibits traces of orthorhombic distortion. The best fit for the $x=6.34$ sample was obtained with $|J_{1D}|/k=1.15$ K, $|J_{2D}|/k=0.41$ K, and $r=0.60$. As for the $x=6.12$ sample, the best parameters were $|J_{1D}|/k=1.11$ K, $|J_{2D}|/k=0.37$ K, and $r=0.80$. It is interesting to note that the interaction constants are essentially the same for both cases. It should also be noted that the value for the coupling constant for the orthorhombic $x=6.31$ sample determined by the 2D Ising model is 0.48 K and fairly close to the J_{2D} values of the 2D XY model. Despite the questionable validity of a 1D and 2D hybrid model of these systems, the above results lend support to the idea that the dramatic difference in the heat-capacity data between the tetragonal and the orthorhombic samples is primarily caused by the change in the Er^{3+} ion anisotropy. Similar hybrids of 1D and 2D Ising models were previously introduced by us[9,10] to explain anomalous heat-capacity

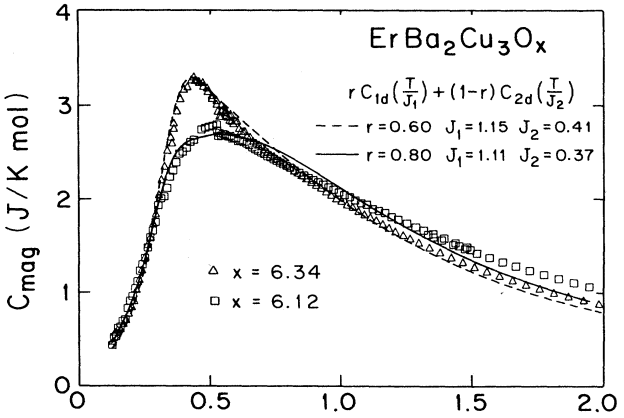

FIG. 9. Magnetic heat capacities of $ErBa_2Cu_3O_x$ with $x=6.12$ (tetragonal) and $x=6.34$ (tetragonal?). Theoretical curves computed for hybrid 1D and 2D XY models are shown together with the fitted parameters as discussed in the text.

curves for several orthorhombic $R\mathrm{Ba_2Cu_3O_x}$ samples with R = Nd, Sm, Gd, and Er.

The reason for one-dimensional behavior in any of these systems is not obvious. One possibility is suggested by studies[37,38] of randomly diluted 2D Ising-like antiferromagnets whose heat capacity and susceptibility increasingly come to resemble those of a linear chain as the percolation limit is approached. A similar effect was also observed for a 3D XY-like system.[39] One might speculate that removal of oxygen from the $R\mathrm{Ba_2Cu_3O_7}$ lattice introduces significant randomness in the magnetic coupling of Er^{3+} moments, i.e., bond dilution and disorder, leading to a similar chainlike linkage within large clusters of interacting spins. Such disordering becomes significant for smaller defect concentrations in 2D than in 3D systems. The 2D XY system might be expected to be particularly sensitive even to small numbers of bond disruptions. Whether in this process one could also account for the apparent tendency toward mixed 1D and 2D behavior in these materials is not clear. We find from the data given in Ref. 37 that the effective coupling constant for the diluted system with apparent 1D Ising-like behavior is about 3 times the coupling constant of the undiluted 2D Ising-like system. The ratios $|J_{1D}/J_{2D}|$ in our systems are also very close to 3. It should be noted that the various theoretical models considered above are relevant only if the interactions among ER^{3+} ions are primarily of short range.

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