Crystal-field interaction in the $Gd_xEu_{1-x}Ba_2Cu_3O_{7-\delta}$ superconductors

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We report here experimental data on the crystal-field interaction of gadolinium ions with their environment in $Gd_xEu_{1-x}Ba_2Cu_3O_{7-\delta}$. The ESR spectrum and a Schottky anomaly in the specific heat of dilute samples ($x \ll 1$) indicate the existence of a crystal-field splitting of the $^8S_{7/2}$ ground state of Gd^{3+} ions of about 1.5 K. We discuss the parametrization of the measured splitting in terms of an effective Hamiltonian, and the microscopic origin of the interaction within the framework of a superposition model. Since the single-ion energies involved are of the same order of magnitude as the energies associated with the magnetic ordering of the Gd^{3+} moments in $GdBa_2Cu_3O_{7-\delta}$ ($T_N \cong 2.24$ K), we analyze the effects of the crystal-field interaction on the magnetic transition.

I. INTRODUCTION

Since the discovery[1] of superconductivity above 90 K in $YBa_2Cu_3O_{7-\delta}$ a large number of compounds have been synthesized replacing yttrium by rare-earth ions. Some of them (e.g., Gd, Er, and Dy) carry well-defined magnetic moments that order at low temperatures, giving rise to λ-type anomalies in the specific heat.[2-8] In the case of $GdBa_2Cu_3O_{7-\delta}$ the magnetic anomaly shows a sharp peak[2] at ~ 2.24 K and a large high-temperature tail indicating that a considerable amount of magnetic energy is still present above T_N due to short-range-order effects. In addition, a pronounced shoulder is observed around 1 K. Features like this are common in Gd compounds with similar ordering temperatures,[9-11] e.g., monoclinic Gd_2O_3 ($T_N = 3.5$ K), $GdVO_4$ ($T_N = 2.5$ K), and $GdAlO_3$ ($T_N = 3.87$ K). This shoulder is primarily due to the high degeneracy of the ground state (eightfold) and it is accounted for in a mean-field model for the transition.[9] In magnetic systems like $GdBa_2Cu_3O_{7-\delta}$, where we will show that the crystal-field splitting is comparable with exchange energies, the Néel temperature is shifted[12] and the shape of the magnetic anomaly in the specific heat[10] may also be affected.

We report here a determination of the crystal-field splitting of the ground state of Gd^{3+} ions in dilute $Gd_xEu_{1-x}Ba_2Cu_3O_{7-\delta}$ compounds, based on electron-spin resonance (ESR) and specific-heat measurements.

In Sec. II we describe our experimental results in terms of an effective crystal-field Hamiltonian. In Sec. III we discuss the microscopic origin of the measured parameters, and in Sec. IV we analyze the effects of the crystal-field interaction on the characteristics of the magnetic order of the $GdBa_2Cu_3O_{7-\delta}$ system at low temperatures.

II. EXPERIMENTAL RESULTS

Samples with nominal composition $Gd_xEu_{1-x}Ba_2Cu_3O_{7-\delta}$ were prepared by sintering mixed powders of Eu_2O_3, Gd_2O_3, $BaCO_3$, and CuO in appropriate concentrations. The starting materials were thoroughly mixed in a high-impact ball mill, loosely packed, and allowed to react for 20 h in air at 980 °C. The samples were then ground, pressed into pellets, heated in an oxygen atmosphere at 985 °C, and slowly cooled to room temperature.

For all samples x-ray diffractograms showed the same orthorhombic structure with lattice parameters changing from $a = 3.840(3)$ Å, $b = 3.902(3)$ Å, $c = 11.706(9)$ Å for $EuBa_2Cu_3O_{7-\delta}$ to $a = 3.835(3)$ Å, $b = 3.898(3)$ Å, $c = 11.694(9)$ Å for $GdBa_2Cu_3O_{7-\delta}$.

Measurements of the magnetic susceptibility, using a Faraday balance magnetometer, show that Gd enters the $GdBa_2Cu_3O_{7-\delta}$ lattice in a trivalent state ($4f^7$, $^8S_{7/2}$) with an effective moment $p_{\text{eff}} = 7.9\mu_B$ and an antiferromagnetic Curie-Weiss temperature $\Theta = 4.8$ K. The low value obtained for the ratio $T_N/\Theta = 0.47$ is characteristic of low-dimensional magnetic order,[13] as it is the large tail of the magnetic anomaly of the specific heat above T_N. For Eu^{3+} ions in $EuBa_2Cu_3O_{7-\delta}$ the expected ground state $^7F_0$ is nonmagnetic, but a paramagnetic susceptibility was observed between 100 and 300 K due to the thermal population of the excited multiplets ^7F_J in agreement with previous measurements.[14] After subtracting

this contribution from the susceptibility of samples with $x < 1$, the remaining Curie-like susceptibility was consistent with the free-ion magnetic moment and the nominal concentration of Gd^{3+}.

The ESR spectra of samples with $0.005 \leq x \leq 0.05$ were measured at 9 and 35 GHz from 2 K to room temperature. Since our samples are polycrystalline powders you expect to observe a superposition of spectra from all possible orientations weighed with their probability. Theoretical simulations, superimposing the different resonance lines have been previously reported for Gd^{3+} ions occupying sites with cubic[15,16] and orthorhombic symmetry.[17-19] The spectra for Gd^{3+} ions in orthorhombic symmetry (C_{2v}) can be described by the following spin Hamiltonian,

$$\mathcal{H} = g\mu_B \mathbf{H}\cdot\mathbf{S} + \frac{D}{3}O_2^0(S) + EO_2^2(S) + \text{fourth- and sixth-order terms}\ , \quad (1)$$

where the first term accounts for the Zeeman energy and $O_n^m(S)$ are Stevens operators describing the crystal-field interaction. According to this Hamiltonian the powder spectrum will consist of seven resonance lines. One intense line in the center of the spectrum results from the superposition of the $-\frac{1}{2} \leftrightarrow \frac{1}{2}$ transition plus contributions arising from the collapse of other transitions due to exchange narrowing. In addition to this central line there will be three satellite lines on each side of it, which correspond to the $\pm\frac{7}{2} \leftrightarrow \pm\frac{5}{2}$, $\pm\frac{5}{2} \leftrightarrow \pm\frac{3}{2}$, and $\pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$ transitions. The position of these lines is associated to the divergencies[19] of the probability distribution, $P(H)$, of finding a resonance between H and $H+\delta H$.

If the crystal-field interaction is small relative to the Zeeman energy, first-order perturbation theory is sufficient and second-order terms may be neglected. In our case, however, these terms give rise to an anisotropic $-\frac{1}{2} \leftrightarrow \frac{1}{2}$ transition at 9 GHz. The calculated powder spectrum shows then two divergencies[18,19] with a separation proportional to $D^2/g\mu_B H_0$, with H_0 being the central field. As expected, and observed in our measurements, these features are less important at 35 GHz. In Figs. 1 and 2 the ESR spectrum for $x = 0.05$ (measured at several temperatures) is given for 9 and 35 GHz, respectively. Similar ESR spectra were obtained when the concentration was changed or Eu was replaced by Y in the matrix. At room temperature the central line of the spectrum, measured at 35 GHz, corresponds to a g value of 1.99 (as expected for Gd^{3+} free ions). Broad shoulders on each side of it appeared as a result of unresolved fine structure.

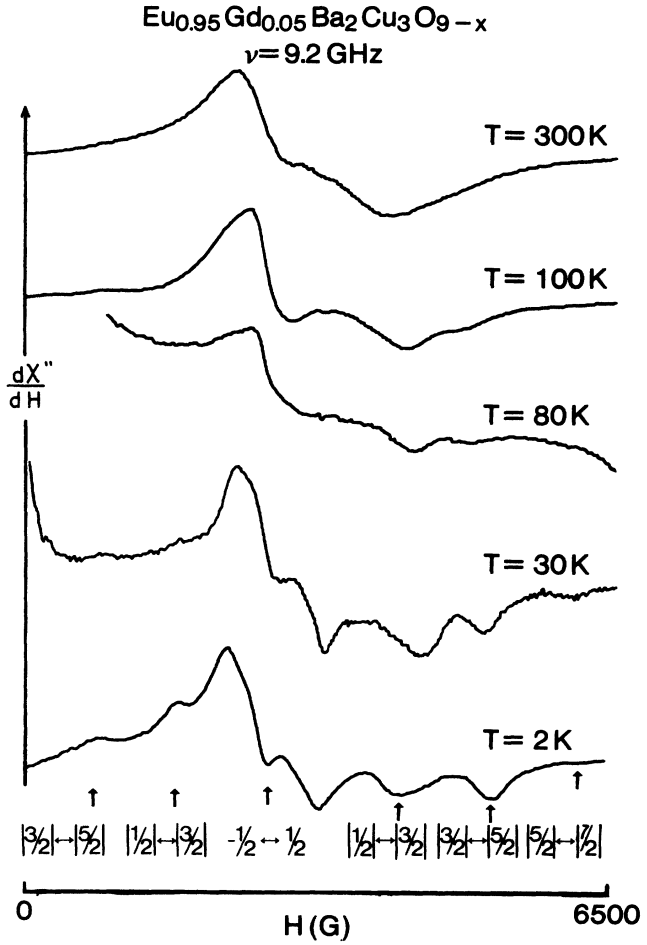

FIG. 1. EPR spectrum at 9.2 GHz for a powder sample of $Eu_{0.95}Gd_{0.05}Ba_2Cu_3O_{7-\delta}$ measured at several temperatures. The arrows indicate the approximate position of the satellite lines.

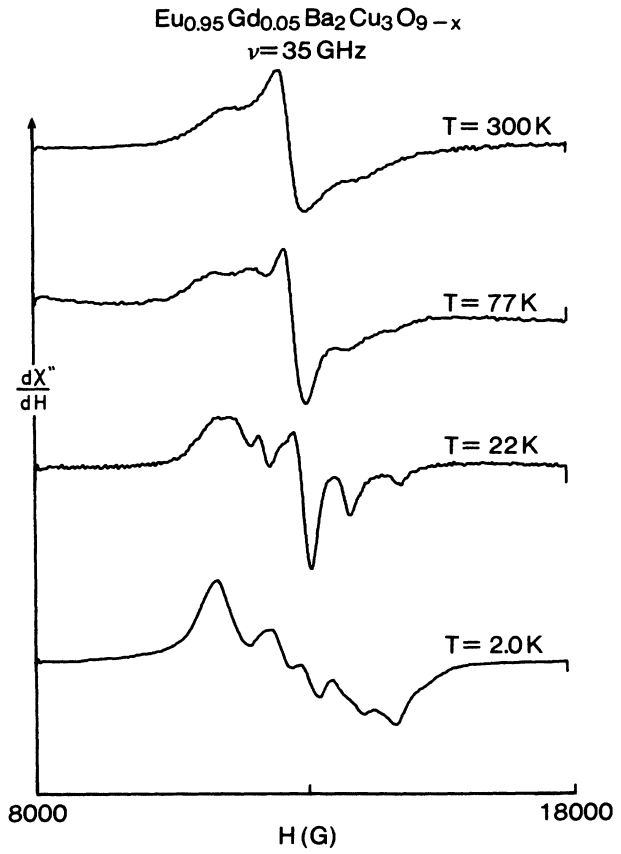

FIG. 2. EPR spectrum at 35.5 GHz for a powder sample of $Eu_{0.95}Gd_{0.05}Ba_2Cu_3O_{7-\delta}$ measured at several temperatures. The arrows indicate the approximate position of the satellite lines.

As the temperature was lowered the satellite lines became more clear at both frequencies. At 9 GHz and for temperatures below the superconducting transition temperature T_c the presence of a field-dependent baseline and the anisotropy of the central line made it very difficult to observe the satellite lines on the low-field side. On the high-field side, three satellite lines were seen as shown in Fig. 3, where a blowup of the 9-GHz spectrum is given for several temperatures.

In the simplest case of axial symmetry where only second-order terms are considered in Eq. (1), three pairs of lines are expected that correspond to the magnetic field perpendicular to the crystal-field symmetry axis. The separation between these lines are $6D$, $4D$, and $2D$, respectively. This is the case of Gd^{3+} ions diluted[18,19] in $SnMo_6S_8$ and $PbMo_6S_8$. On the other hand, when the local symmetry is cubic, two of the three transitions are usually superimposed[15,16] and only two pairs of lines are observed. Although it is not certain from the separation between resonance lines that our data can be analyzed by taking into account only an O_2^0 term in the Hamiltonian, the observation of three separate satellite lines indicate that it is not unreasonable to do so. With this consideration, we obtain from the observed spectra the value $D \simeq 0.13$ K, and consequently a total crystal-field splitting of 1.5 K.

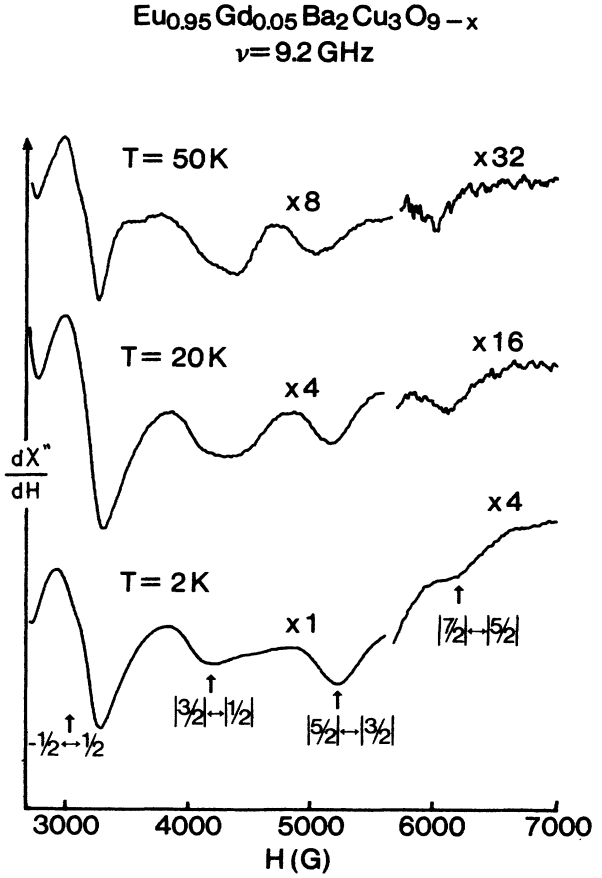

FIG. 3. EPR spectrum at 9.2 GHz for the high-field satellite lines for a powder sample of $Eu_{0.95}Gd_{0.05}Ba_2Cu_3O_{7-\delta}$. Note that the transition $\frac{7}{2} \leftrightarrow \frac{6}{2}$ has been amplified by a factor of 4.

In principle, it should be possible to determine the sign of the crystal-field parameters by analyzing the relative change in amplitude of the different ESR spectral lines as a function of temperature. However, because of the uncertainty on the number of terms that should be included in the Hamiltonian for the crystal-field analysis, and the presence of a low-temperature absorption line[20] superimposed to the crystal-field ESR spectrum, we prefer to be cautious about this subject, knowing that this issue will be clarified when single crystals become available.

It is apparent from Figs. 1 and 2 that the fine structure is narrowed with increasing temperature especially for $T \geq T_c$. The narrowing process for a given fine structure is essentially governed by the impurity conduction electron relaxation rate,[21] which also contributes to the temperature dependence of the individual fine-structure linewidths. The increase of the linewidths with temperature[22] is of the order of 1 G/K for $T > T_c$ uncovering a small interaction between the local moments and the conduction electrons.

The specific heat of dilute compounds was measured with a semiadiabatic calorimeter down to 0.45 K. The temperature dependence showed a broad anomaly with a maximum that shifts to higher temperatures with increasing Gd concentration, as shown in Fig. 4. In the case of the most dilute sample, $x = 0.02$, the specific heat has a low-temperature upturn without reaching its maximum value within the measured temperature range; see Fig. 5. We associate this feature with the high-temperature tail of a Schottky anomaly originating in the crystal-field splitting of the eightfold degeneracy of the ground state of Gd^{3+} ions. The shift of the maximum towards higher temperatures in more concentrated samples is probably related to the presence of short-range magnetic ordering of the Gd moments. A detailed analysis of the concentration dependence of the specific heat is in progress and will be reported elsewhere.

From the specific-heat data for the sample with $x = 0.02$, after subtracting the nonmagnetic contribution of the matrix, we have estimated the crystal-field contribution to the measured specific heat. A comparison with

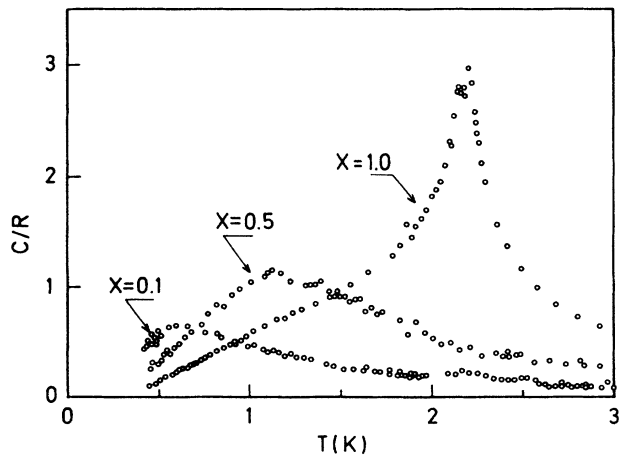

FIG. 4. Specific heat of $Gd_xEu_{1-x}Ba_2Cu_3O_{7-\delta}$ per mole of Gd.

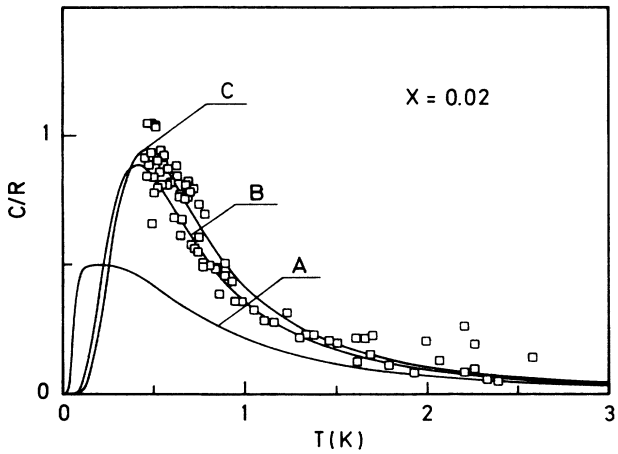

FIG. 5. Specific heat of $Gd_{0.02}Eu_{0.98}Ba_2Cu_3O_{7-\delta}$ and calculated crystal-field Schottky anomaly for $D=+0.13$ K (curve A), $D=-0.13$ K (curve B), and $D=-0.13$ K, $b_4^0=-0.00785$ K (curve C).

the Schottky peak calculated with the Hamiltonian of Eq. (1) and the value of D derived from the ESR experiment is shown in Fig. 5 assuming $D>0$ (curve A) or $D<0$ (curve B). It is seen that only curve B reproduces closely the measured values. The inclusion of calculated higher-order contributions, to the crystal-field Hamiltonian (curve C), as discussed in the next section, does not affect the agreement observed.

III. SUPERPOSITION MODEL FOR THE CRYSTAL FIELD

The nonzero values of the crystal-field interaction in the ${}^8S_{7/2}$ ground state of Gd^{3+} ions is a consequence of a very small admixture with excited states with nonzero orbital angular momentum. Since the microscopic mechanisms that lead to this effect arise from high-order perturbations, it is extremely difficult to carry out *ab initio* derivations of the measured crystal-field splittings. However, it is possible to analyze the experimental results using a semiempirical approach called the superposition model.[23] It is based on the hypothesis that the measured effects can be described as the sum of independent contributions from each of the surrounding ions. In this model the crystal-field parameters are related to a reduced number of "intrinsic"[23] parameters $\bar{b}_2(R)$, $\bar{b}_4(R)$, and $\bar{b}_6(R)$ characteristic of each type of ligand that depend on the ligand distance R. The measured parameters are determined by explicit functions of the angular coordinates of the ligands grouped in shells at distances R_a.

In the case of the $RBa_2Cu_3O_{7-\delta}$ structure the R ions are surrounded by a shell of eight oxygen atoms located in the corners of a slightly distorted cube. For perfect cubic symmetry it is always true that the second-order parameters vanish:

$$D=\bar{b}_2\sum_i \tfrac{1}{2}(3\cos^2\theta_i-1)=0$$

and

$$E=\bar{b}_2\sum_i \tfrac{3}{2}\sin^2\theta_i\cos 2\phi_i=0\ ,$$

and only fourth- and sixth-order terms in (1) have nonzero values.

For the distorted oxygen cube surrounding the rare-earth ions in $EuBa_2Cu_3O_{7-\delta}$ nonzero values are obtained for the second-order angular factors. Using the value $\bar{b}_2=-0.17$ K, estimated by Newman and Urban[23] for the interaction with oxygen ligands (with an accuracy of $\pm$ 50%) we have calculated a contribution, $D=-0.04$ K. This calculated value agrees in sign and order of magnitude with the specific-heat data, indicating that about one third of the second-order crystal-field interaction may be attributed to the interaction with the nearest oxygen ions.

The calculated anisotropic second-order term E is very small ($E=b_2^2=0.004$ K), in agreement with the assumed parametrization of the experimental data. In the case of fourth-order parameters an estimate of their magnitude can be made if we assume that they also originate mainly from the interaction of Gd^{3+} ions with the surrounding oxygen atoms. This environment is similar to that found for Gd^{3+} impurities[24] in ThO_2 and CeO_2, where the crystal-field Hamiltonian has only fourth- and sixth-order terms, due to the cubic symmetry of the impurity sites:

$$\mathcal{H}_{\text{cubic}}=B_4[O_4^0+5O_4^4]+B_6[O_6^0-21O_6^4]\ . \qquad (2)$$

Since the Gd-O distances are almost the same we expect for $EuBa_2Cu_3O_{7-\delta}$ similar values of B_4^m corrected for the angular distortions of the oxygen cube. Including these corrections (which are less that 5%) we estimate a value of $B_4^0=-0.00785$ K; B_6^0 is even smaller. Since the O_2^0 term is dominant in Eq. (1), the higher-order terms can be taken into account as a perturbation and only the diagonal part needs to be estimated. The inclusion of these terms increases the crystal-field splitting and shifts the calculated specific-heat anomaly to higher temperatures, as shown in Fig. 5 (curve C).

IV. CRYSTAL-FIELD EFFECTS ON THE MAGNETIC ORDER OF $GdBa_2Cu_3O_{7-\delta}$

The crystal-field interaction is a single-ion effect causing magnetocrystalline anisotropy in magnetic systems, determining preferred orientations for the sublattice magnetization in the case of antiferromagnetic ordering. A negative value of D indicates the existence of an easy axis of magnetization [z axis referred to Eq. (1)] and a positive value of D an easy plane perpendicular to it. In the $GdBa_2Cu_3O_{7-\delta}$ system the negative value derived from the specific-heat data would favor magnetization parallel to the crystal-field z axis, coincident with the c axis of the crystal structure. However, calculations carried on for classical moments interacting through dipole-dipole interactions[25] show that the ground state for a simple orthorhombic lattice corresponds to an antiferromagnetic order with the moments lying in the a-b plane, if $c\gg a,b$. This result indicates that dipolar and crystal-field energies represent competing interactions. Unfortunately a comparison cannot be made with independent evidence derived from Mössbauer experiments because the interpretations given by different authors to their data[26,27] are not in agreement with each other.

Other crystal-field effects to be expected are a shift of the transition temperature[12] ΔT_N and a change in the shape of the low-temperature shoulder of the specific heat.[10] In order to discuss these effects we have included our axial crystal-field values into a mean-field calculation of the magnetic transition. We have found that the spontaneous magnetization reaches almost its saturation value at temperatures around $T_N/2$, and at lower temperatures the energy-level scheme does not greatly differ from that of a single ion in a fixed applied magnetic field, giving rise to a shoulder in the specific heat. Although the crystal-field interaction modifies the relative spacing of the energy levels our experimental value of $|D| \sim 0.13$ K implies only minor changes in the intensity of the shoulder leaving almost unchanged the overall shape of the specific-heat anomaly. We conclude that the low-temperature feature of the specific heat is, as in other Gd compounds,[9] a consequence of the high-spin degeneracy and is not influenced much by the crystal field. This indicates that there is only a single-ordering process in the entire temperature range measured.

The calculated shift of the transition temperature T_N is small ($\pm$ 15% for $D = \pm 0.13$ K), thus not affecting our comment in Sec. II on the low dimensionality of the magnetic lattice in $GdBa_2Cu_3O_{7-\delta}$ based on the ratio $T_N\Theta$.

V. CONCLUSIONS

We have determined the second-order axial contribution to the crystal-field interaction for Gd^{3+} ions diluted in $EuBa_2Cu_3O_{7-\delta}$ from ESR and specific-heat measurements. Following a semiempirical approach we have found that a significant contribution to this interaction arises from the distorted cube of oxygen ions that surround the rare-earth ion. Assuming that the measured crystal-field interaction is not greatly changed in samples with higher Gd concentrations, we have discussed its effect on the magnetic order of the concentrated magnetic system ($GdBa_2Cu_3O_{7-\delta}$).

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