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CRYSTAL FIELD INTERACTION AND MAGNETIC ORDER IN $GdBa_2Cu_3O_7$

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We report experimental data on the crystal field interaction of Gd ions with their environment in $Gd_xEu_{1-x}Ba_2Cu_3O_7$. The ESR spectrum and a Schottky anomaly in the specific heat of dilute samples indicate the existence of a crystal field splitting of the $^8S_{7/2}$ ground state of the Gd^{3+} ions of about 1.5K. Since the single ion energies involved are of the same order of magnitude as the energies associated with the magnetic ordering of the Gd moments in $GdBa_2Cu_3O_7$ (T_N = 2.24K) we analyze the effects of the crystal field interaction on the magnetic transition.

Many of the recently discovered superconducting oxides, $ABa_2Cu_3O_7$, (with A = Y or rare earths) show coexistence of superconductivity and magnetic order at low temperatures /1,2/. It is then of interest to characterize the type of magnetic order present in these materials and to study the interrelation of this order with the superconducting properties.

We report here a calorimetric and electron spin resonance (ESR) study of the crystal field interaction of Gd^{3+} ions in the $ABa_2Cu_3O_7$ structure, and we analyze its effects on the magnetic order of the $GdBa_2Cu_3O_7$ compound. We have measured pure $GdBa_2Cu_3O_7$ and dilute samples of $Gd_xEu_{1-x}Ba_2Cu_3O_7$ with $0.005<x<0.05$, where we have chosen $EuBa_2Cu_3O_7$ as a non-magnetic host in order to separate the single ion interactions of Gd atoms.

The samples were prepared by sintering thoroughly mixed powders of Eu_2O_3 Gd_2O_3, $BaCO_3$ and CuO, in appropriate concentrations. The raw materials were allowed to react in air for 20 hours 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 in the same atmosphere.

Measurements of the specific heat were made down to 0.45K using a semi-adiabatic calorimeter. The specific heat of $GdBa_2Cu_3O_7$ presents a lambda type anomaly peaked at 2.24K, in agreement with previous reports /1/. In the case of dilute samples, the magnetic contribution to the measured specific heat was obtained after substraction of the specific heat of the $EuBa_2Cu_3O_7$ host.

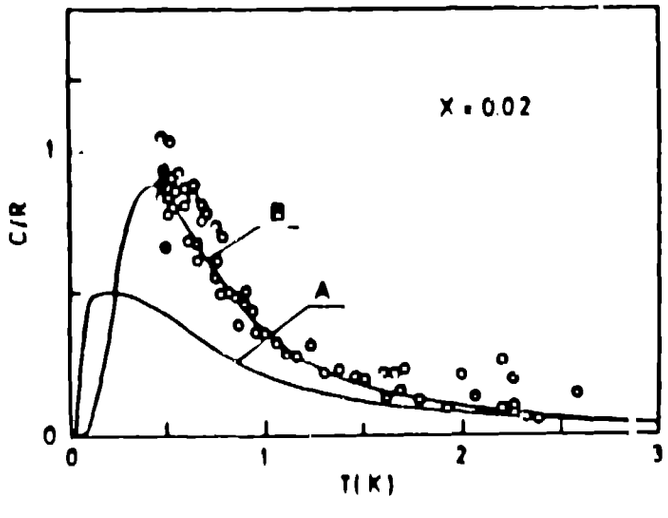

Fig. 1. Specific heat of $Gd_{0.02}Eu_{0.98}Ba_2Cu_3O_7$.

A low temperature upturn was observed for samples of low concentration as shown in Fig.1 for x = 0.02. We have associated this feature with the high temperature tail of a Schottky anomaly due to the crystal field splitting of the ground state of Gd^{3+} ions, based on the results of ESR measurements as we discuss below.

The ESR spectra of powdered polycrystalline samples with $0.005<x<0.05$ were measured at 9 GHz and 35 GHz from 2K to room temperature. At the lowest temperatures a spectrum with resolved fine structure was obtained as shown in Fig.2 for x = 0.05. This spectrum has a central line around g = 2 and satellite lines at both sides.

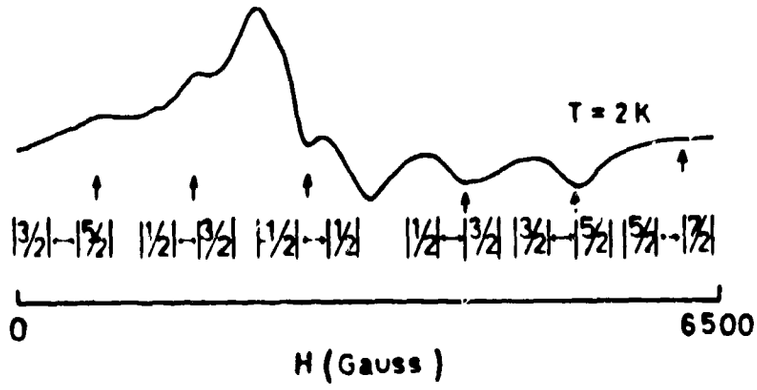

Fig.2. ESR spectrum for $Gd_{0.05}Eu_{0.95}Ba_2Cu_3O_7$ measured at 9 GHz.

The spectrum of powdered samples is expected to show a superposition of lines arising from all the possible orientations of the particles relative to the applied magnetic field. Theoretical simulations have been reported /3,4/ for Gd^{3+} for two cases: cubic and axial symmetries. In the first case four separate satellite line have been observed experimentally and six in the case of axial symmetry. The number of separate lines observed in our samples and their relative spacing allowed us to describe the spectrum with a simple effective Hamiltonian:

$$\mathcal{H} = (D/3)\{3S_z^2 - S(S+1)\} \qquad [1]$$

Although this Hamiltonian is appropriate for axial or tetragonal (C_{4v}) symmetry and the Gd sites in $ABa_2Cu_3O_7$ have orthorhombic (C_{2v}) symmetry, the deviation from tetragonal symmetry is very small and the proposed Hamiltonian is expected to give a reasonable description of the experimental results. By fitting the position of the ESR lines to this Hamiltonian we have obtained a value of $|D/k_B| = 0.13K$. This value of the crystal field parameter would give rise to a total crystal field splitting of about 1.5K and a Schottky anomaly in the specific heat as shown in Fig.1 for a positive (curve A) and a negative (curve B) value for D.

When the Gd magnetic moments order in the concentrated system $GdBa_2Cu_3O_7$ the crystal field interaction causes anisotropy in the magnetic properties. A negative value of D favors, at T = 0K, ordering of the magnetic moments parallel to the symmetry axis of the crystal field interaction, and a positive value of D favors ordering in the plane perpendicular to it. The negative value of D suggested by the interpretation of our specific heat data in terms of the simple crystal field Hamiltonian of Eq.1, would indicate magnetic order along the c axis. However, classical dipole-dipole interactions should

also be considered, not only as a source of magnetic anisotropy, but rather as a possible cause for the magnetic order itself. In this case antiferromagnetic order is expected /5/ with the Gd moments forming ferromagnetic chains alligned along the a-axis. Mössbauer spectroscopy of ^{155}Gd ions should in principle provide experimental evidence concerning the relative orientation of the magnetic moments with respect to the symmetry axes of the electric field gradient at the Gd site, which in turn is related to the crystal field interaction. Unfortunately, a comparison with existing experimental data is difficult because the interpretations given by different authors /6,7/ are not unique.

The shape of the specific heat anomaly as a function of temperature is also expected to depend on the crystal field field interaction. In cases where this interaction is much larger than the magnetic energies involved in the ordering process, its main effect is to partially remove the degeneracy of the free ion ground state. This is the case of the $ABa_2Cu_3O_7$ compounds with A = Dy or Er, where only a Kramers doublet remains populated at the temperatures where magnetic order takes place /8/. In the case of A = Gd, and because Gd^{3+} is an S-state ion, the crystal field interaction is much weaker and its effects are noticeable around T_N. Our experimental data for $GdBa_2Cu_3O_7$ are shown in Fig.3, in comparison with the specific heat of $GdVO_4$, a typical antiferromagnetic compound /9/ with similar Neel temperature (T_N = 2.5K). At high temperatures a large specific heat tail indicates that short-range magnetic order is important well above T_N , and at low temperatures a shoulder is observed, which is characteristic of many magnetic compounds containing Gd atoms /10/. This shoulder is primarily due to the high degeneracy (8-fold) of the ground state of Gd^{3+} ions /10/. In our case, the shoulder appears around 1K, where thermal energies are of the same order of magnitude as the crystal field interaction.

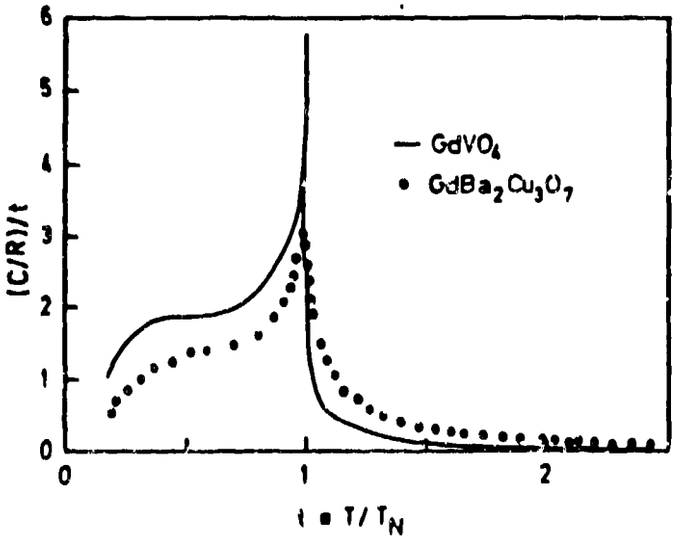

Fig.3. Specific heat for $GdBa_2Cu_3O_7$. For comparison it is also shown the specific heat of the antiferromagnetic compound $GdVO_4$.

In order to analyze the effects of this interaction on the specific heat temperature dependence, we have carried out a mean field calculation of the magnetic transition including an axial crystal field term, as given by Eq.1. It was observed in this model that at temperatures below $\sim T_N/2$, the energy levels are almost temperature independent and equally spaced in absence of crystal field interaction. This gives rise to the low temperature shoulder in the specific heat, as shown in Fig.4, where we display C/T vs. temperature in order to visually enhance the presence of the shoulder. Our mean field

calculation shows that for our experimental value of D, only minor changes in the overall shape of the specific heat are expected, with a shift of the transition temperature of about 15%, as shown in Fig.4.

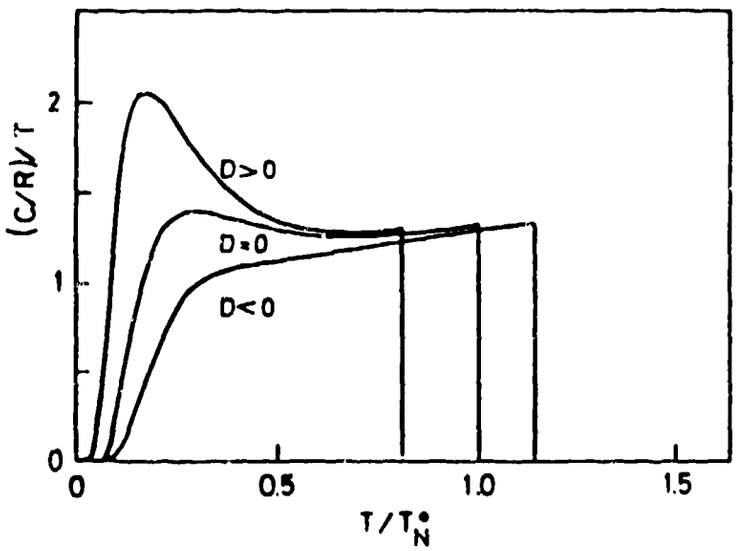

Fig.4. Mean field calculation of the magnetic anomaly of the specific heat for different values of the crystal field parameter D. The molecular field parameter has been chosen to give the measured Neel temperature for D = 0.

In conclusion, we have obtained a coherent description for the ESR and specific heat data of dilute samples, using a simple crystal field Hamiltonian with axial symmetry. From this simple model it follows that the crystal field parameter should be negative in order to fit the specific heat data. This is also consistent with the shape of the low temperature shoulder observed for the concentrated system $GdBa_2Cu_3O_7$.

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