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Electron paramagnetic resonance of Gd^{3+} ions in the superconductor $GdBa_2Cu_3O_x$

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EPR from Gd^{3+} ions in the high-$T_c \simeq 90$ K superconductor $GdBa_2Cu_3O_x$ is reported. The temperature dependence of the linewidth and intensity of the Gd^{3+} ions in the vicinity of T_c are related to the corresponding characteristics of the Cu^{2+} ions.

Recently[1] we reported the observation of electron paramagnetic resonance from Cu^{2+} ions in the multiphase superconductor $Y_{0.2}Ba_{0.8}CuO_x$ with $T_c \simeq 90$ K. The signal linewidth was temperature independent in the high-temperature region but showed a slight decrease at $T \gtrsim T_c$ and an increase for $T < T_c$. The signal intensity exhibited a Curie-like behavior at $T \gg T_c$, a Pauli-like flattening at $T \gtrsim T_c$, and a sharp increase for $T \lesssim T_c$. The g value was temperature independent throughout the observed region. We have since observed similar signals with the same linewidth and intensity characteristics in nominally single-phase $Y_1Ba_2Cu_3O_x$ superconductors, although the signal intensity in the latter case is much weaker than that in the multiphase sample. In this paper we report on the paramagnetic resonance of Gd^{3+} ions in the superconductor (Ref. 2) $GdBa_2Cu_3O_x$. The resonance characteristics in the vicinity of T_c appear to be related to those of the Cu^{2+} ions.

The material was fired at 850 °C for 12 h in helium and annealed in flowing oxygen for ~ 16 h. The resistivity measurements showed superconductivity with midpoint at 87 K and with a width $\Delta T = 2$ K. The magnetic moment, measured in a field of 14 G as a function of temperature, showed a gradual drop beginning at 92 K. At 4.5 K the volume susceptibility was -0.03 compared to the theoretically expected value of ~ -0.11. Therefore, we deduce that about 27% of the sample exhibits diamagnetic shielding. When cooled from above T_c in a field of 14 G, a Meissner effect of $\sim$42% of the superconducting portion is observed, which is typical of low-density ceramic specimens.[3]

X-band resonance spectra at various temperatures are shown in Fig. 1. The spectrum consists of a single, slightly asymmetric line of width greater than 1000 G. The asymmetry, which is quite small as compared with even poor metals, is temperature independent. Metallic resonance signals usually exhibit a Dysonian line shape, which is distinctively asymmetric. Such line shapes arise because metals have a complex surface impedance, and are expected when the skin depth is smaller than the grain size of the sample. That the line shape is only slightly asymmetric for a bulk sample indicates that the sample consists of quite small grains. Further, the line shape does not change as a function of temperature suggesting that the asymmetry is not due to a complex surface impedance. An asymmetric line shape can also be associated with spin diffusion in concentrated magnetic systems, with internal field distributions, or with unresolved fine and hyperfine structures. We believe that the latter is the most likely source of the observed asymmetry.

The g value of 1.97 ± 0.01 is temperature independent. The negative g shift from the unshifted $g \simeq 2$ contrasts with the positive shift for Gd^{3+} impurity resonance in $YBa_2Cu_3O_x$ reported by Shaltiel *et al.*[4] and is opposite in sign to the corresponding shifts in most metals. However, it is consistent with the negative shifts observed for Gd substituted in both Pt and Pd which, like the present material, leaves the Gd interacting with almost filled d bands and for which there is a very small $5d$ density of states at the Gd site. The positive g shift is usually associated with the intra-ion interaction between the $4f$ and $5d$ electrons.[5]

The linewidth variation with temperature is shown in Fig. 2. Unlike the Cu^{2+} ions, which showed a temperature independence for $T \gg T_c$, the Gd^{3+} linewidth at high T shows a conventional linewidth variation, increasing with temperature due to the Korringa interaction.[6] A rate of ~ 1 G/K follows if we interpret the linear rise between 100 and 200 K as being due to this mechanism. This is consistent with the observed[3] Barnes-Plefka[7] narrowing of the single-ion spectrum. The relaxation time for narrowing is proportional to, but roughly an order of magnitude larger than, the Korringa relaxation rate. Between 200 to 300 K the linewidth fails to linearly increase with increasing temperature. This may be interpreted as a competition between the Barnes-Plefka narrowing and the Korringa broadening.

For $T \lesssim T_c$ the linewidth behavior is quite similar to that for the Cu^{2+} resonance.[1] The reason for the increase in linewidth with T_c is far from clear. It is not consistent with the internal field distribution produced by the vortex lines. As a measure of the width of this distribution one might take the difference in the field at the center of a vortex and that at the saddle point. This goes with H_{C2}/κ^2 where κ is the ratio of the London penetration depth of ~ 2000 Å to the coherence length of ~ 15 Å. The estimate of Bezinge, Jorda, Junod, and Muller[8] of $H_{C2} \sim 300$ kG at 86 K gives a width of about 7.5 G, which is an order of magnitude too small to explain the observed change of width. More important is the complete absence of an associated line shift. Therefore, we speculate that the change in linewidth is caused by whatever mechanism is responsible for the line intensity rise in the same temperature range (see below).

The temperature variation of the signal intensity is shown in Fig. 3. For $T \gg T_c$, the behavior is consistent with the expected Curie-Weiss law and a plot of the in-

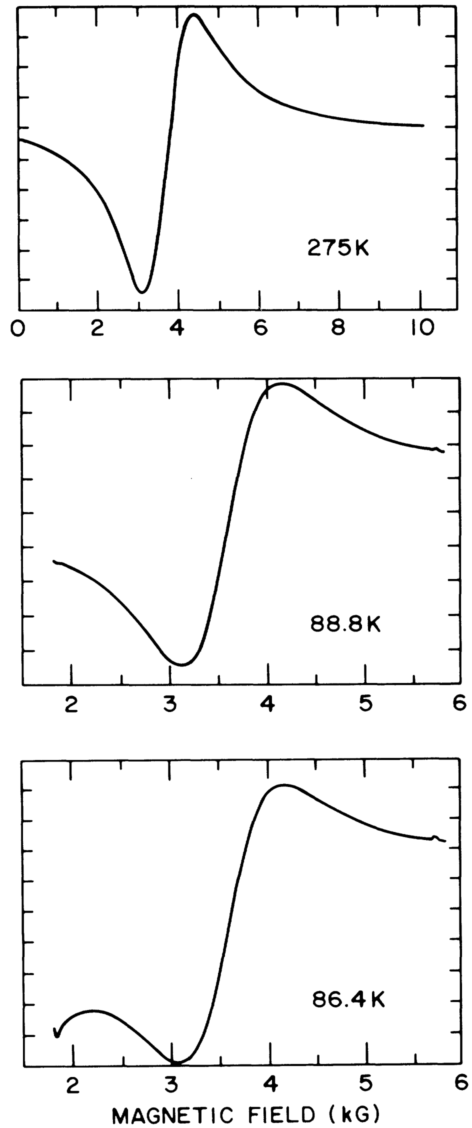

FIG. 1. X-band EPR spectra of Gd^{3+} in $GdBa_2Cu_3O_x$ at various temperatures.

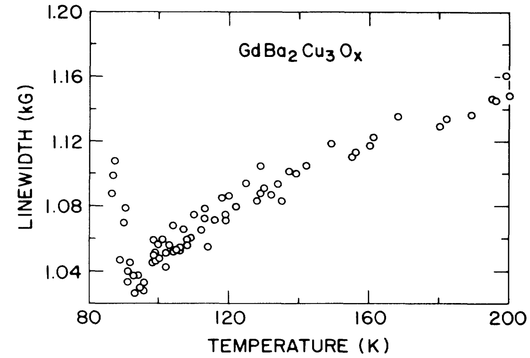

FIG. 2. Temperature variation of the EPR linewidth. The linewidth at room temperature is ~1180 G.

verse intensity versus temperature leads to a negative $\Theta = -30$ K. However, upon decreasing the temperature to the vicinity of T_c the strength first fails to increase as fast as the high-temperature Curie-Weiss law would predict and then upon decreasing T below T_c there is a sharp rise until at about 80 K the signal intensity is greater than that expected from the Curie-Weiss law. Qualitatively the Cu^{2+} resonance[1] was similar except both the flattening and sharp increase were much more pronounced. Therefore, it is natural to associate these common features with the same cause. It is not difficult to find a mechanism by which the signal intensity close to T_c might rise with decreasing T more slowly than expected. For example, it now seems to be widely accepted that the superconductivity is granular in the high-T_c ceramics of the type studied here. In such a picture, some of the grains must become superconductive before the appearance of bulk superconductivity, i.e., for $T \gtrsim T_c$. In the field for resonance approximately 3300 G, the static field is easily large enough to put the material in the type-II regime. However, assuming the flux lines are even modestly well pinned, the small microwave field will only enter the London penetration depth, which is estimated to be ~2000 Å. As the grains become superconductive the signal will be lost from those grains with an effective dimension, which is greater than this (temperature dependent) depth. The first deviations from linear resistance typically occur at about 115 K consistent with the flattening of the signal strength. The problem with such a granular model is that it cannot explain the sudden increase in strength below T_c.

It is also tempting to associate the relatively small changes in intensity observed here with a Cu^{2+} component of the signal. In considering such a model it should be noted that the present ESR is that of a concentrated system whereas that studied by Shaltiel *et al.*[4] is a dilute alloy with Gd substituted for Y. Their g shift of ~0.05 is quite large and positive and may be attributed to the Gd^{3+}-Cu^{2+} interaction. In the concentrated Gd system, however, the two submagnetizations cannot exert a torque on each other and as a result there is no mutual g shift. With this interpretation the increase in strength

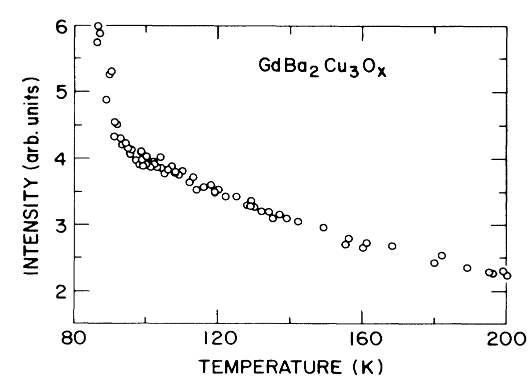

FIG. 3. Temperature variation of the EPR line intensity. The intensity at room temperature is ~1.4.

below T_c reflects the previously observed[1] strong increase in the magnetization of the Cu^{2+} subsystem. However, the observed g factor of a joint resonance is the susceptibility weighted average

$$g_{\rm eff} = \frac{g_{\rm Cu}\chi_{\rm Cu} + g_{\rm Gd}\chi_{\rm Gd}}{\chi_{\rm Cu} + \chi_{\rm Gd}} \ .$$

In order to explain the increased intensity below T_c it would be implied that $\chi_{\rm Cu} \sim (0.1-0.3)\chi_{\rm Gd}$ at the lowest temperature observed. For Cu^{2+} we take the average $g_{\rm Cu}=2.08$ and for Gd^{3+} $g_{\rm Gd}=1.97$, from the high-temperature data. As the weighting of the Cu moment increases below T_c there should be a g shift of $\sim 0.01-0.03$, which is within detectable limits. No such shift is observed.

We are, therefore, led to associate the behavior around T_c with changes in the conduction-electron properties. Such an interpretation requires some notions about the nature of the Cu^{2+} ionic state and the superconductivity. For this reason what follows is speculative.

Since our original ESR measurements on the yttrium compound, it has become increasingly clear that the best superconducting materials have Pauli rather than Curie-Weiss susceptibilities. Consistent with this view, we have observed that the existence of the magnetic moments observed in our ESR experiments, and for that matter susceptibility measurements, is *very* sensitively dependent upon treatment. Since the changes that the material undergoes during annealing are evidently quite subtle, and, it is likely related to the concentration and placement of the oxygen, it is not probable that all (or most) of the magnetic Cu^{2+} ions change valence or that the electronic correlations could be modified sufficiently to convert the magnetic Cu^{2+} ions ($U > \Delta$) into nonmagnetic Cu^{2+} ions ($U < \Delta$), where U is the effective Coulomb repulsion and Δ is the effective $3d$ bandwidth. It seems more natural to assume that during annealing, the material is rendered more uniform and that this results in all of the intrinsically magnetic Cu^{2+} ions (with spin $\frac{1}{2}$) being "compensated" by some means. Anderson[9] has suggested that this compensation takes the form of resonant valence bonds (RVB) while we have suggested[1] that it arises via the Kondo effect. If, as is the case in mean-field theory, the RVB pairing is absent above T_c the system should go from paramagnetic to the (partially) compensated RVB state at T_c. Whatever the exact nature of the change at T_c, within a more realistic non-mean-field theory, it would seem on physical grounds that the formation of Cu-Cu spin pairs in this fashion would lead to a decrease in the average Cu^{2+} moment upon entering the superconducting state. In contrast, because there is a gap associated with the superconductivity below T_c, the onset of superconductivity tends to cut off infrared divergences and thereby inhibits Kondo compensation, i.e., in our picture the Cu^{2+} moment will *increase* at T_c in agreement with ESR experiments. Within this picture, because it is somewhat disordered, the yttrium compound has a distribution in Kondo temperatures. It is those ions with lower Kondo temperatures, and therefore the larger moment in a field, which are observed in ESR. We have estimated a typical $T_K \gtrsim 100$ K.

The Gd^{3+} ion with spin $\frac{7}{2}$ is evidently not compensated and, hence, the much smaller changes in intensity for this ion are to be associated with more subtle changes in the conduction electrons. Specifically, a part of the Gd-Gd interaction must be mediated by the polarization of conduction electrons on the Cu. The onset of the Kondo effect is associated with the appearance of a resonance in the density of state on the Cu. It follows that there will be a concurrent increase in the Gd-Gd interactions and the Weiss Θ and thereby a decrease in the Curie-Weiss susceptibility and, hence, the resonance strength. As superconductivity suppresses the Kondo compensation the opposite is true and the strength increases sharply.

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