Paramagnetic resonance of Cu^{2+} ions in the superconductor $Y_{0.2}Ba_{0.8}CuO_x$

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A strong paramagnetic resonance signal characteristic of Cu^{2+} ions in $|x^2-y^2\rangle$ states is observed in the high-$T_c \approx 90$ K superconductor $Y_{0.2}Ba_{0.8}CuO_x$. The line intensity of the ioniclike signal shows a deviation from Curie behavior at $T \gtrsim T_c$. It is speculated that the phase that is responsible for the signal is an example of an Anderson lattice with an unusually high Kondo temperature.

Unlike the original[1] La-based high-T_c superconducting cuprates in which no Cu^{2+} paramagnetic resonance signal is observed in any phase, the Y compound[2] $Y_{0.2}Ba_{0.8}CuO_x$ shows a strong resonance spectrum (Fig. 1) reminiscent of those observed in insulating cooperative Jahn-Teller Cu^{2+} compounds.[3] The powder spectra in Fig. 1 are due to the Cu^{2+} ions in tetragonal sites in the state:[3]

$$|2^s\rangle \equiv \frac{1}{\sqrt{2}}(|+2\rangle + |-2\rangle) \equiv |x^2-y^2\rangle \ .$$

The measured g values are $g_\perp = 2.033 \pm 0.002$; $g_\parallel = 2.193 \pm 0.004$.

From the theory of Bleaney, Bowers, and Pryce[4] the anisotropic g values (up to first order) are given by $g_\parallel = 2 + 8\lambda/\Delta_0$; $g_\perp = 2 + 2\lambda/\Delta_1$, where λ is the spin-orbit parameter and Δ_0 and Δ_1 are, respectively, the energy differences between the ground $|x^2-y^2\rangle$ state and the excited $|xy\rangle$ and the degenerate $|yz\rangle$; $|zx\rangle$ states. The linewidth (Fig. 2), taken to be the separation between the left maximum and minimum (Fig. 1), is essentially temperature independent from room temperature down to 100 K. In the vicinity of T_c there is a slight dip while the linewidth increases quite significantly below T_c. Whatever might be the precise origin of the linewidth,[5] it is evident that the resonance signal comes from a region of the sample which "sees" the superconductivity, either directly or indirectly, perhaps by the proximity effect.

The material was fired at 950 °C for 12 h. The resistivity measurement showed a superconductivity onset at 107 K, completed at 84 K with the midpoint at 89.8 K and ΔT

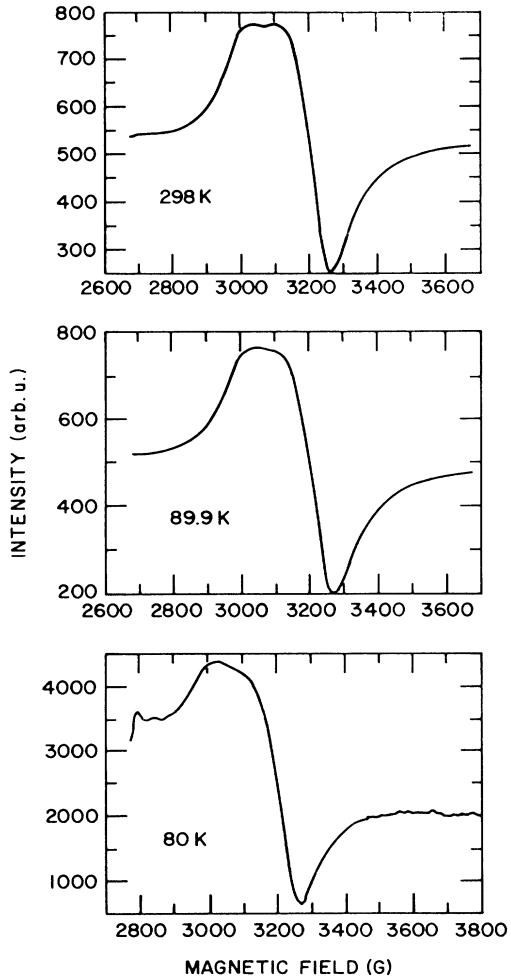

FIG. 1. X-band EPR spectra of Cu^{2+} in $Y_{0.2}Ba_{0.8}CuO_x$ at various temperatures.

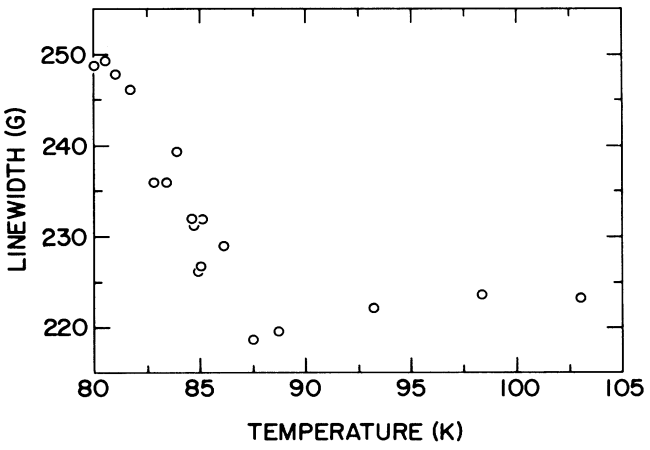

FIG. 2. Temperature variations of the EPR linewidth. The linewidth at room temperature is ~226 G.

(from 10% to 90%) = 3.7 K. At high temperatures the resistivity is $\approx 1000\ \mu\Omega$ cm. The magnetic moment was measured in a field of 13.9 G as a function of temperature showing a sharp drop at 88 K. The initial moment at 4.5 K gave a volume susceptibility of -0.016 as compared to the theoretically expected value of ≈ -0.09 if the whole sample was superconducting, i.e., only $\sim 18\%$ of the sample exhibits diamagnetic shielding. When the sample is cooled from above T_c in the same field, a Meissner effect of $\approx 75\%$ of the superconducting portion is observed which is surprisingly high. From the linearity of magnetic moment versus magnetic field plot at 4.5 K, a critical field $H_{c1} \approx 500$ G was determined.

The sensitivity of the EPR spectrometer is calibrated by using a paramagnetic standard of known spin density. With the usual large uncertainty associated with absolute ESR intensity measurements, the signal intensity (i.e., the difference between the numbers of spins parallel and antiparallel to the magnetic field) is $\sim 10^{18}$ spins/g at room temperature. More reliable than the absolute strength is the measurement of the relative intensity shown in Fig. 3 (defined as the peak-to-peak amplitude multiplied by the square of the linewidth). The intensity rises slowly for $T \gg T_c$, flattens for $T \gtrsim T_c$, and sharply rises below T_c. The theory of Bleaney, Bowers, and Pryce[4] is appropriate only for ionic Cu^{2+}, i.e., when this ion has a local moment. If this were the situation, then the signal would exhibit a Curie susceptibility and should change by a factor of 3 between 300 and 100 K. Clearly no such temperature dependence is observed. On the other hand, if the signal at $T \gtrsim T_c$ is associated with the Pauli paramagnetism of the Cu states near the Fermi surface, then it is relevant to consider the band-structure calculations of Mattheiss.[6] He estimates the carrier density to be $\approx 10^{22}/\text{cm}^3$. A rough estimate of the associated Pauli paramagnetic signal intensity is given by multiplying this density by $\frac{1}{2}(h\nu\rho)$, where ρ is the density of states[6] ≈ 1.32 (eV)$^{-1}$ and $\nu \approx 9.3$ GHz is the microwave frequency. With a density of ≈ 3.6 g/cm^3 this gives an intensity of $\sim 7 \times 10^{17}$ spins/g, indicating that the observed intensity is consistent with that expected for CESR (conduction electron spin resonance).

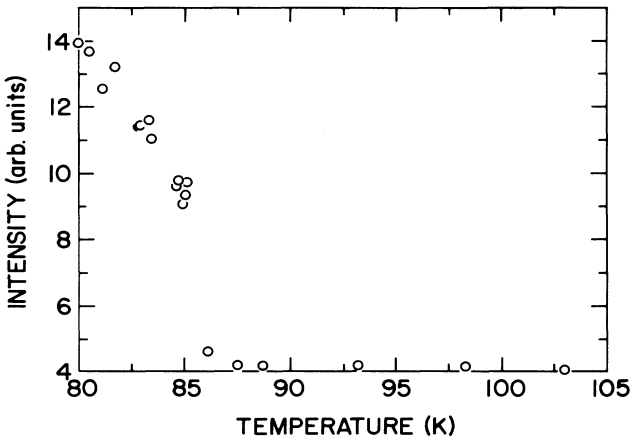

FIG. 3. Temperature variation of the EPR line intensity. The intensity at room temperature is ~ 2.

It has been established[7] that the superconducting phase of these compounds has the formula $YBa_2Cu_3O_x$. The Cu^{2+} EPR signal has to come from a metallic phase (whether or not superconducting) to have a Pauli-like susceptibility at $T \gtrsim T_c$. To explain the observed signal as being ordinary CESR is difficult. Very few CESR signals can be seen at room temperature due to rapid spin relaxation. For example,[8] for Al, Ag, or pure Cu, above 30 K this rapid relaxation is due to phonon-induced spin-orbit scattering and leads to a linewidth which increases rapidly with temperature. Since, as evidenced by the observed g-factor anisotropy, the spin-orbit coupling here is not small and since it is unlikely that the electron-phonon coupling is minuscule, it is difficult to understand how the linewidth can be temperature independent over such a wide range above T_c. Furthermore, impurity and phonon scattering invariably averages out g-factor anistropies so that only the Fermi-surface average is relevant at higher temperatures. No anisotropy in the g factor is observed in the above-mentioned cubic metals. The only CESR in a noncubic metal, of which we are aware, is that of Mg which also has an isotropic g factor within experimental error.[9]

The possibility of the signal coming from Cu^{2+} ions in the vicinity of defects can be excluded since such signals would be much weaker than observed and would have a Curie-like temperature dependence. Even if it would be possible to explain the temperature variation of the resonance strength, it is very unlikely that the signal could correspond to ordinary paramagnetic Cu^{2+} local moments in normal metals. A great number of perovskite-related compounds have been studied.[10] An examination of these indicates clear trends associated with the formation of local moments. Local moments do occur in $KCuF_3$ where the Cu^{2+} has strongly electronegative ligands. The Co in $LaCoO_3$ has a local moment, while $LaNiO_3$ is reported to have a temperature-independent susceptibility in the range 77 to 575 K, indicating the absence of such a moment. On the other hand, La_2NiO_4 exhibits a Curie-Weiss susceptibility with a negative (antiferromagnetic-like) $\Theta = -500$ K. No magnetic ordering is observed down to 100 K. $La_2Li_{0.5}Ni_{0.5}O_4$ exhibits a Jahn-Teller effect associated with the local moment on Ni^{3+}. The system $La_{1-x}Sr_xCoO_3$ is also of interest. In this material the Co may undergo a local to itinerant transition for an x of approximately 1.25. These trends indicate that the compounds La_2BO_4 form a sequence in which Co and Ni have local moments while Cu does not. The other perovskites indicate that the tendency of an ion to exhibit a local moment can be altered by passing through the sequence of compounds between ABO_3 and A_2BO_4 and/or by varying the composition in the materials $A_xA'_{1-x}BO_y$ where A and A' have different valences.

Whether a local moment exists or not depends upon the relative magnitude of the effective Coulomb repulsion denoted by U and the degree of covalent mixing associated with a parameter $\Delta = \rho V^2$, where ρ here is the effective density of states of the conduction electrons in an Anderson lattice[11] and V is the mixing interaction between Cu and O ligands. The degree of covalency will depend upon

the nature of the ligand as is evidenced by the existence of a Cu^{2+} moments for strongly ionic materials. In the present context the effective Coulomb repulsion is the energy required to add one electron, from the Fermi surface, to Cu^{2+} to make it Cu^{1+}. Both experimental and theoretical experience with the dilute magnetic alloy problem shows that this latter quantity varies smoothly across the $3d$ series decreasing steadily towards the end as the empty d level approaches the Fermi surface. Invariably for $3d$ ions in elemental metals Cu is nonmagnetic because the $3d$ levels lie well below the Fermi surface. Local moments therefore disappear in the sequence Fe-Co-Ni. Here the energetics are such that $3d$ levels of Cu are almost certainly not full. For a given perovskite A_xBO_y the relevant sequence in which the moment disappears will now be Co-Ni-Cu. As with the dilute alloy, in mixed-valent or heavy fermion problems whether or not a Curie-Weiss law is observed depends upon the temperature range involved. In this sense La_2NiO_4 might be mixed valent with a characteristic (or Kondo) temperature of 500 K. The evidence thus suggests that Cu in the present material may be characterized as having a local moment with $U > \Delta$ but with an unusually high Kondo temperature, i.e., these Cu-based high-T_c superconductors are mixed-valent systems corresponding to something like an Anderson lattice.

The theory of the Anderson lattice is still in its infancy and very little is known about its ESR properties. However, the perturbation scheme is known[12] and this alone indicates that the present observations are more consistent with this model than with the conventional CESR picture discussed above. Since U is the larger energy, the first step in the mixed-valent scheme is to treat the atomic correlations and only then to include the covalent mixing with the ligands, i.e., in this scheme the $3d$ levels would be treated according to the ionic theory of Bleaney *et al.*[4] In particular, the spin-orbit coupling is included in this initial stage and is reflected by an anisotropic g factor as described above. The coupling of spin orbit to phonons will result in only a small modulation in the anisotropic g shifts. The temperature variation of the linewidth in this case should be similar to those in insulators where experiment[3] suggests that it is negligible up to room temperature. Adding the covalent mixing causes the Cu^{2+} moment to be Kondo compensated resulting in a deviation from Curie-like towards Pauli-like susceptibility below the Kondo characteristic temperature. This ionic scheme is known[5] to work for the non-mixed-valent rare-earth ions in dilute solution even when the splittings of the ionic configuration are very much smaller than Δ. Even for mixed-valent Ce it seems to be widely accepted that structure in general, and crystal-field structure in particular, will be ioniclike if the relevant splitting exceeds the Kondo temperature rather than the much larger Δ. In the present case the crystal field levels which are coupled by the spin-orbit coupling, and lead to the anisotropic g factor, are separated by about 1 eV in insulators which is bigger than a reasonable estimate for the lattice Kondo temperature $\gtrsim 100$ K.

In summary, we have observed the ESR characteristic of ionic Cu^{2+} except that the strength of the resonance above and near T_c shows a temperature variation away from Curie-like and towards Pauli-like dependence. We have not been able to account for this temperature dependence of the intensity of the ioniclike signals by conventional explanations and have therefore speculated that the phase which produces the signal may be an example of an Anderson lattice with a large Kondo temperature of $\gtrsim 100$ K.

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