Title
Absence of Cu2+ electron-spin resonance in high-temperature superconductors and related insulators up to 1150 K

Journal
Physical Review B, 48(6)

ISSN
2469-9950

Authors
Simon, P
Bassat, JM
Oseroff, SB
et al.

Publication Date
1993-08-01

DOI
10.1103/physrevb.48.4216

RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 48, NUMBER 6 1 AUGUST 1993-II

Absence of Cu^{2+} electron-spin resonance in high-temperature superconductors and related insulators up to 1150 K

P. Simon and J. M. Bassat
Centre de Recherche sur la Physique des Solides, CNRS, 45071 Orléans Cedex 2, France

S. B. Oseroff
Physics Department, San Diego State University, San Diego, California 92182

Z. Fisk
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

S-W. Cheong
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

A. Wattiaux
Laboratorie de Chimie du Solide, CNRS, Université de Bordeaux I, 33405 Talence Cedex, France

Sheldon Schultz
Physics Department, University of California, San Diego, California 92093
(Received 7 May 1993)

One unresolved question in the high-temperature superconductors and their copper oxide parent compounds is the absence of a Cu^{2+} electron-spin-resonance (ESR) signal even at temperatures well above the Néel temperature. We have extended the measurements up to 1150 K in both single crystals and ceramic pellets of $La_2CuO_{4+\delta}$, $0 \lesssim \delta \lesssim 0.12$, and no ESR signal has been observed. Our data are not compatible with the models based only on magnetic fluctuations which predict an ESR linewidth of a few hundred Oe at such high temperatures. Other suggested explanations for the absence of a Cu^{2+} ESR signal are discussed.

The absence of a Cu^{2+} electron-spin-resonance (ESR) signal for temperatures up to 570 K has been reported previously by us[1] and other investigators[2,3] in the copper oxide superconductors and their parent compunds. As the ESR signal of the Cu^{2+} is one of the easiest to observe, at least in insulators, its absence is intriguing. It has been shown that in those reports where an ESR signal has been attributed as intrinsic to the high-T_c superconductors, the signals observed are in fact due to the presence of impurity phases.[1-3]

The nature of ESR in other two-dimensional antiferromagnetic (2D-AF) compounds has been studied in several systems, and an ESR signal is observed only above T_N.[4] The general behavior is that from temperatures of $\sim 3T_N$ the linewidth decreases slowly as the temperature is reduced, passes through a minimum at $\sim 2T_N$, and subsequently increases anomalously when approaching T_N from above. Since the 3D ordering temperature is ~ 300 K for the R_2CuO_4 ($R \equiv$ La, Pr, Nd, etc.) systems, the fact that a Cu^{2+} ESR signal was not observed at temperatures up to ~ 570 K in these compounds suggests that the 2D-AF correlations are strong even for $T \sim 2T_N$, or that there are other mechanisms that broaden the Cu ESR signal beyond detectable limits.

Soon after the discovery of high-T_c superconductivity, Anderson[5] proposed that these systems, when not doped, behave as 2D-AF with localized copper-oxygen hybrid centers of $S = \frac{1}{2}$. The existence of such entities has been experimentally confirmed by different techniques including NMR,[6] muon-spin resonance,[7] and neutron scattering.[8] Several authors have shown that the magnetic properties of these compounds can be described by a Heisenberg AF model with $S = \frac{1}{2}$ and a coupling constant J of ~ 1500 K.[8] The interplanar coupling has been reported to be only $\sim 10^{-5}J$.[9] Thus, strong 2D-AF quantum fluctuations are present in the paramagnetic region where most of the experimental data are usually taken.

Several tentative explanations have been proposed for the nonobservance of an ESR Cu^{2+} signal in the high-T_c superconductors and their insulating parent compounds. Charkravarty and Orbach[10] calculated the ESR linewidth (ΔH) for La_2CuO_4. They proposed that ΔH is severely broadened by anisotropic exchange, and with decreasing temperature increases as $(\xi_{2D}/\mathbf{a})^3$, where ξ_{2D} is the 2D spin-correlation length and $\mathbf{a}$ is the lattice constant. They estimated a Cu^{2+} ESR signal which is very broad at room temperature, but measurable with conventional ESR spectrometers at 600 K, $\Delta H \lesssim 4$ kOe. Recently Lazuta[11] included weaker anisotropic forces, besides the Dzyalosinskii-Moriya (DM) interactions, and concluded that the contribution to linewidth due to the DM interaction decreases with increasing temperatures, as $\xi_{2D}/\mathbf{a}$, whereas the contribution associated with the weaker sym-

0163-1829/93/48(6)/4216(3)/$06.00

metric anisotropic forces varies as $(\xi_{2D}/\mathbf{a})^3$. The values of ΔH estimated in Ref. 11 are 2.7 kOe at 300 K and 0.6 kOe at 400 K, which should be easy to observe. Lazuta suggested a different mechanism based on the presence of holes in the CuO_2 planes due to oxygen nonstoichiometry[11] which could inhibit the presence of the Cu^{2+} signal. He suggests the need to study high-quality samples, with $T_N \gtrsim 300$ K, to assure oxygen stoichiometry. It should be mentioned that by either varying the oxygen content or appropriate doping, both T_N and ξ_{2D} can be reduced, thereby making it easier to observe the ESR lines at lower temperatures, while still being in the range of the linewidth minimum at $T \sim 2T_N$.

Another explanation for the absence of a Cu^{2+} signal is that the Cu^{2+} ions form pairs with an $S=0$ ground state.[12] These pairs would constitute the basic entities of the short-ranged resonance valence bond (RVB) state.[5] As such pairs would have an $S=1$ triplet excited state, their presence should be easy to observe in high-temperature magnetization measurements. Also, doublet ESR signals from the $S=1$ excited state may be seen at high temperature. To the best of our knowledge no experimental support for an $S=1$ excited state has been reported in the literature.[13]

At this point it is not clear that any of the models proposed is able to explain the absence of the Cu^{2+}. Thus we felt that systematic ESR measurements in $La_2CuO_{4+\delta}$ in both high-quality ceramic and single-crystal samples should be made to still higher temperatures. In particular measurements at temperatures of the order of the coupling constant J, where $\xi_{2D} \sim 0$, could be particularly valuable in guiding the search for the explanation of this puzzle.

The measurements were performed at 9.2 GHz in a Varian spectrometer between 2 K and 570 K. A Bruker system, also operating at 9.2 GHz and specially designed to take measurements at high temperature, was used between 300 K and 1150 K. The samples are held in a silica tube, the outer part of which is heated by a hot gas flow. Temperatures of the order of 1300 K can be reached with the system. The Q factor of the resonant cavity is basically temperature independent, at least up to 1150–1200 K. This was verified by monitoring the Cu^{2+} signal of the green phase Y_2BaCuO_5. We found that the integrated intensity of the Cu^{2+} ESR signal followed a $1/T$ law, consistent with the Curie susceptibility expected for an insulating compound at high temperature.

Experiments were carried out in high-quality single crystals of La_2CuO_4.[14] The crystals as grown have a T_N, as measured by dc magnetization, of ~ 260 K. When these crystals were vacuum annealed at ~ 900 K for 48 h, their T_N increased to ~ 320 K. *None of the crystals studied, as grown or vacuum annealed, showed an ESR signal between 2 K and 1150 K.* A similar negative result was obtained in ceramic samples with a $T_N \sim 310$ K. We have also performed measurements on $La_2CuO_{4.12}$ ceramic pellets. These unusually high values of oxygen content were obtained by electrochemical oxidation in an alkaline medium.[15] These samples show superconductivity at $T_c \sim 40$ K. Thus, there is no 3D-magnetic order, i.e., $T_N = 0$. Measurements in these compounds also showed *no ESR signal up to 720 K.* The highest temperature at which reliable data were taken in the high-oxygen ceramic compounds was limited to 720 K because noise, possibly due to electric losses associated with the mobility of the oxygens in the superoxygenated sample, make the data unreliable above that temperature. Our system allows one to choose the gas at the modest pressures around the sample, but it is not possible to apply the very high oxygen pressure needed to maintain high values of δ upon heating. The samples were checked by x-ray magnetization, before and after the ESR experiments were done. No changes in their properties were found.

The absence of a Cu^{2+} ESR signal up to 1150 K in single crystals, and ceramics with $\delta \simeq 0$, suggests that models which predict that the ESR linewidth decreases with increasing temperature as a certain function of ξ_{2D} cannot explain the experimental data. The most conservative estimate of such models furnishes a value for ΔH of ~ 200 Oe at 1000 K,[10,11] which should lead to a very intense signal, definitively not present in any of the samples we have studied. For example, an equal amount of the green phase Y_2BaCuO_5 gives an $S/N \gtrsim 1000$ with a $\Delta H \simeq 300$ Oe at 1000 K. Thus we could have seen a signal with a linewidth up to ~ 3 kOe with an $S/N \gtrsim 10$. The data taken in the superconducting $La_2CuO_{4.12}$ samples, where a large reduction of ξ_{2D} is expected, do not support these models either. The ESR Cu^{2+} line would be easier to observe in the superoxygenated samples, if ΔH was, as claimed, only a function of ξ_{2D}.[10,11] Lazuta's suggestion that the absence of an ESR signal is due to the presence of holes is not supported by the data. No ESR signal was found in the vacuum-annealed samples which should have a negligible number of holes. Further evidence against this argument are data taken in a larger number of single crystals of R_2CuO_4 ($R \equiv$ Pr, Nd, Sm, Eu), with $T_N \sim 270$ K, which are close to stoichiometry and also do not show a Cu^{2+} signal at temperatures up to 650 K.[16]

Finally, the explanation that the absence of an ESR signal is a manifestation of an $S=0$ ground state, is not compatible with the nonobservance of an ESR signal for the $S=1$ excited state. It is also contradicted by our magnetization measurements up to 1000 K in samples of La_2CuO_4 from the same batch. Instead the magnetization data are consistent with the presence of $S=\frac{1}{2}$ centers, in agreement with previous measurements published by other groups.[2,17] In summary, none of the models reported in the literature explain the absence of an ESR signal up to temperatures of the order of the exchange coupling J. We suggest that other relaxation processes contribute to the linewidth besides magnetic fluctuations.

We would like to present a possible explanation for the absence of an ESR signal in $La_2CuO_{4+\delta}$ and the other copper oxides. As mentioned before, several other 2D-AF $S=\frac{1}{2}$ salts had been studied by ESR more than two decades ago.[4] In the case of $Cu(HCOO)_2 \cdot 4H_2O$, with an interaction between Cu^{2+} ions in the planes of ~ 90 K and $T_N \sim 17$ K the temperature dependence of the resonance linewidth had been fitted to[18,19]

$$\Delta H(T) = a + bT + c(\xi_{2D}/\mathbf{a})^n , \quad (1)$$

where the first term is the residual linewidth, extrapolated to $T=0$ K from the paramagnetic region, i.e., $kT>J$. The second term, bT, is valid for $T \gtrsim 2T_N$. Both contributions had been explained as due to phonon modulation of the Dzialoskinsky-Moriya interaction.[18] It has been argued that the large values of J and the DM interaction in this salt lead to the linear temperature dependence observed above $2T_N$. This dependence is not found in other magnetic salts wih smaller values of J and negligible DM interaction.[4,18] Similar to other 2D-AF systems the linewidth for this Cu salt goes through a minimum at $\sim 2T_N$ and increases rapidly when approaching T_N. This critical region[19] has been fitted to a term proportional to $(\zeta_{2D}/\mathbf{a})^n$, with $n \sim 2.5$, which is in good agreement with magnetic fluctuation models.[10,11] Kindo *et al.*[20] observed the ESR line for CuO using a pulsed high field technique. This is a useful technique when detecting very broad resonances. Other groups, using conventional ESR spectrometers, tried unsuccessfully to observe this signal.[3] This is an important result because CuO can be placed in the same class of materials as the high-T_c copper systems and their parent compounds. The overall temperature dependence of the resonance linewidth of CuO is similar to that observed for $Cu(HCOO_2)\cdot 4H_2O$. But, each of the three terms of Eq. (1) is much larger in the CuO case. For CuO the residual linewidth, extrapolated from $T>T_N$ is ~ 13 kOe. The minimum, which occurs at $T>T_N$, is ~ 14 kOe and the linewidth increases almost linearly with temperature above this minimum at a rate of ~ 60 Oe/K. It is interesting to note that the values of J and DM are much larger for CuO than for $Cu(HCOO_2)\cdot 4H_2O$, but smaller than for La_2CuO_4 and its parent compounds. So it is likely that there is a simple explanation for the nonobservance of the Cu signal: its linewidth is too broad to be observed at any temperature, at least with conventional ESR spectrometers.

Finally, we like to refer to an exotic "mechanism" suggested recently by Mehran.[13] He argues that the $S=\frac{1}{2}$ entities are not fermions but are anyons in a chiral spin liquid state. If the spin $=\frac{1}{2}$ centers are anyons, they would not obey time-reversal symmetry, and would not be Kramers degenerate. The lines may then become too broad to be detected by conventional ESR techniques.[21] Still, this "anyon state" and its associated chiral liquid state has been estimated to fall into a normal state at temperatures of the order of $J, \sim 1500$ K,[22] close to the highest temperature we measured.

In conclusion, the absence of a Cu^{2+} ESR signal up to 1150 K in samples with different oxygen content contradicts the models based only on magnetic fluctuations as well as other tentative explanations used to explain the nonexistence of a Cu^{2+} signal. We suggest that the experimental results presented here should be taken into account when proposing models to explain the interplay between magnetism and superconductivity in the high-temperature superconductors.

This research was partially supported at San Diego State University by the National Science Foundation under Grant No. NSF-DMR-9117212, at Los Alamos National Laboratory under the auspices of the United States Department of Energy, and at The University of California San Diego by Grant No. NSF-DMR-89-15815.

[1]D. Vier *et al.*, Phys. Rev. B **36**, 8888 (1987), and references therein.

[2]F. Mehran and P. W. Anderson, Solid State Commun. **71**, 29 (1989).

[3]F. Mehran *et al.*, Solid State Commun. **67**, 1187 (1988); F. Mehran *et al.*, *ibid.* **76**, 55 (1988).

[4]P. M. Richards and M. B. Salamon, Phys. Rev. B **9**, 32 (1974); J. E. Gulley *et al.*, J. Appl. Phys. **40**, 1318 (1969); M. S. Seehra and T. G. Castner, Phys. Kondens. Mater. **7**, 185 (1968).

[5]P. W. Anderson, Science **235**, 1196 (1987).

[6]C. H. Pennington *et al.*, Phys. Rev. B **39**, 2902 (1989).

[7]Y. J. Uemura *et al.*, Phys. Rev. Lett. **59**, 1045 (1985); A. Weidinger *et al.*, *ibid.* **62**, 102 (1989).

[8]G. Shirane *et al.*, Phys. Rev. Lett. **59**, 1613 (1987); Y. Endoh *et al.*, Phys. Rev. B **37**, 7443 (1988); G. Aeppli *et al.*, Phys. Rev. Lett. **62**, 2052 (1989); K. Yamada *et al.*, Phys. Rev. B **40**, 4557 (1989); R. R. P. Singh *et al.*, Phys. Rev. Lett. **62**, 2736 (1989).

[9]R. J. Birgeneau and G. Shirane, in *Physical Properties of High Temperature Superconductors,* edited by D. M. Ginsberg (World Scientific, Singapore, 1989), and references therein.

[10]S. Chakravarty and R. Orbach, Phys. Rev. Lett. **64**, 224 (1990).

[11]A. V. Lazuta, Physica C **181**, 127 (1991).

[12]S. A. Kivelson *et al.*, Phys. Rev. B **35**, 8865 (1987); K. W. H. Stevens, Czech. J. Phys. **41**, 819 (1991); W. R. McKinnon *et al.*, Solid State Commun. **66**, 1093 (1988).

[13]F. Mehran, Phys. Rev. B **46**, 5640 (1992).

[14]C. Rettori *et al.*, Phys. Rev. B **47**, 8156 (1993).

[15]J. C. Grenier *et al.*, Physica C **173**, 139 (1991).

[16]S. B. Oseroff *et al.*, Phys. Rev. B **40**, 1934 (1990).

[17]T. R. McGuire, Phys. Rev. B **36**, 4032 (1987); D. C. Johnston, Phys. Rev. Lett. **62**, 957 (1989).

[18]T. G. Castner, Jr. and M. S. Seehra, Phys. Rev. B **4**, 38 (1971).

[19]T. G. Castner, Jr. and M. S. Seehra (private communication).

[20]K. Kindo *et al.*, J. Phys. Soc. Jpn. **59**, 2332 (1990).

[21]A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970).

[22]B. I. Halperin *et al.*, Phys. Rev. B **40**, 8726 (1989); X. G. Wen *et al.*, *ibid.* **39**, 11 413 (1989).