Anyon explanation for the absence of divalent-copper EPR in high-temperature superconductors and related insulators

F. Mehran
IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, New York 10598
(Received 13 January 1992)

Easy detectability of spin-$\frac{1}{2}$, orbitally nondegenerate centers by electron paramagnetic resonance follows from the existence of Kramers degeneracy, which is a consequence of time-reversal symmetry. If the spin-$\frac{1}{2}$ centers in high-temperature superconductors and related insulators are not fermions but are anyons, they will not obey time-reversal symmetry, their spin doublets will be split by inhomogeneous internal local fields, and their EPR may then not be easily detectable.

Immediately after the discovery of superconductivity in copper oxides,[1] Anderson[2] proposed that these magnetically "two-dimensional" compounds contained localized copper-oxygen hybrid centers with spins $\frac{1}{2}$ which played an important role in the mechanism for superconductivity. The existence of these centers has been amply verified by many experimental techniques such as NMR[3] and neutron scattering,[4] and their importance in understanding the nature of the superconducting process is generally accepted. Since it is almost certain that the spin-$\frac{1}{2}$ centers are present, it has been quite puzzling[5] that they are totally invisible to the standard spectroscopy that can directly detect them, i.e., electron paramagnetic resonance (EPR). To be sure, there are many examples in the literature where the observation of relatively weak Cu^{2+} signals have been reported in isolated cases in these compounds. However, the nature of the Cu^{2+} EPR lines is such that if they are present, they will be enormous and ubiquitous, as they are in the green-phase[6] Y_2BaCuO_5. Many explanations have been proposed to account for the absence of Cu^{2+} EPR, but none of them are very convincing:

(a) In the metallic phases, the Kondo effect,[7] spinon-holon scattering,[5] and heavy-fermion–light-fermion interactions[8] have been invoked. However, all these mechanisms are dependent on the existence of conduction electrons, which is apparently not necessary to quench the signals that are also absent in the insulating counterparts. Therefore, the reason must be deeper and one should not complicate the problem by first considering the metallic state. It is much simpler to concentrate on the insulators La_2CuO_4, $YBa_2Cu_3O_6$, and especially the simplest insulator, CuO.[9]

(b) In the insulating phases, many authors have accepted the EPR absence as a manifestation of the resonating valence bond (RVB) states[2] which are constructed from spin-$\frac{1}{2}$ pairs with $S=0$ ground states. This is certainly not justified because at high temperatures (as high as 570 K) where EPR has been sought, there is no difference between the long-ranged RVB (Ref. 2) state and the ordinary paramagnetic state. Short-ranged RVB,[10] or any dimer state with $S=0$ ground states, should have easily accessible $S=1$ excited states that would probably be visible to EPR. It has been proposed[11] that the zero-field splittings of the $S=1$ manifold may be large enough to prevent the observation of EPR even at very high fields. However, the predicted magnetic susceptibility from these latter states does not agree with experiment.[9] In fact, all high-temperature experiments are consistent with an ensemble of spin-$\frac{1}{2}$ states and not with dimers of any kind.

(c) Since it is well established that at high temperatures these compounds can be accurately described as being magnetically two-dimensional [with intraplane exchange about 10^5 times larger than the interplane exchange], it has been proposed[5,12,13] that in the insulators, two-dimensional magnetic fluctuations persist at high temperatures and the EPR linewidths vary as some function of the magnetic correlation lengths. This explanation is also not convincing for the following reasons:

(i) The most conservative estimate is that of Chakravarty and Orbach[12] who, not knowing the correlation functions, have made several approximations based on various theories and admit to having overestimated the fluctuation effects, and yet, according to their estimate, the EPR linewidth for La_2CuO_4 at 570 K should be at most 5 kG. A simple calculation based on the sensitivity of our apparatus shows that the signal with this linewidth would be strong enough to be detected. Lazuta's analysis[13] yields a linewidth of 600 G at 400 K for La_2CuO_4.

(ii) By varying the oxygen contents, the Néel temperatures and correlation lengths can be drastically reduced, making the lines even easier to see at high temperatures. No line has been seen[14–16] even when $T_N \rightarrow 0$.

(iii) Although ordinary EPR has not been detected in any of the black-phase insulators, Kindo *et al.*,[17] in an important paper, have reported the observation of pulsed magnetic resonance in CuO; the linewidth is 16 kG at room temperature. This is direct evidence that the localized spin-$\frac{1}{2}$ centers postulated by Anderson[2] are actually present, at least in CuO. The reason that they are difficult to see is not that they are not there, but that the EPR lines due to them are unusually and enormously wide. But the most important aspect of their report is that the linewidth, except in the close vicinity of T_N, *in-*

creases with temperature, in contradiction with the magnetic fluctuation theories[5,12,13] that predict sharp *decreases* in linewidths with increasing temperatures.

Not being totally satisfied with any of these complication explanations, one of course would like to find a simple explanation for this persistent mystery. A possible simple (though exotic) explanation can be found if these spin-$\frac{1}{2}$ entities are not fermions but are anyons in a chiral spin liquid state.[18-22] The basic requirement for the easy observability of the EPR of spin-$\frac{1}{2}$ orbitally nondegenerate centers is the existence of Kramers degeneracy which is a consequence of time-reversal symmetry. Non-Kramers degeneracies,[23-26] in general, are not easy to detect because they are split by local random fields which vary from site to site and broaden the EPR line. The reason that spin-$\frac{1}{2}$ centers, such as those in the divalent copper, are ordinarily so easily detectable in the paramagnetic state, is that the Kramers degeneracies (in fermions) are completely immune to local crystal fields, strains, defects, Jahn-Teller, spin-orbit, spin-spin, or any other internal time-reversal-symmetric interactions. To split them, one has to introduce a time-reversal-antisymmetric interaction. This is ordinarily achieved by the Zeeman interaction, i.e., by applying an external magnetic field which is in general highly uniform; thus all centers are split equally. If the spin-$\frac{1}{2}$ centers are not fermions but are, because of magnetic two-dimensionality, anyons, they will not obey time-reversal symmetry, there will be no Kramers degeneracy, and the lines may become too broad to be easily detectable by ordinary EPR. At the same time, this absence of Kramers degeneracy for the spin-$\frac{1}{2}$ electrons would not strongly affect other experiments such as NMR and neutron scattering that indirectly detect them. While the temperature below which the chiral spin liquid state sets in (if it does) is not known, it is believed (by anyon advocates)[18-22] that it would be of the order of the antiferromagnetic exchange parameter ($\sim$1000–1500 K), which is higher than the highest temperature used in the EPR experiments ($\sim$570 K).

The explanation proposed in this paper, of course, does not prove the existence of anyons. It simply points out that if they exist, the spontaneous breaking of time-reversal symmetry, caused by two-dimensional spin statistics, would cause the EPR lines to be widened by internal fields as they usually are in non-Kramers doublets and the temperature dependence of their linewidths will be consistent with what has been observed in cupric oxide[17] which contradicts all previous explanations.

The "negative" EPR results discussed in this paper are, so far, the only experiments that are consistent with the existence of anyons in two-dimensional copper oxides. The only "positive" evidence for their existence, i.e., the observation of circular dichroism,[27] appears to have been invalidated by subsequent experiments.[28]

The author has benefited from stimulating discussions with Dr. D. H. Lee, Dr. C. B. Hanna, and Professor P. W. Anderson.

[1]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).
[2]P. W. Anderson, Science **235**, 1196 (1987).
[3]C. H. Pennington, D. J. Durand, C.P. Slichter, J. P. Rice, E. D. Bukowski, and D. M. Ginsberg, Phys. Rev. B **39**, 2902 (1989).
[4]J. M. Tranquada, G. Shirane, B. Keimer, S. Shamoto, and M. Sato, Phys. Rev. B **40**, 4503 (1989).
[5]F. Mehran and P. W. Anderson, Solid State Commun. **71**, 29 (1989).
[6]F. Mehran, S. E. Barnes, E. A. Giess, and T. R. McGuire, Solid State Commun. **67**, 55 (1988).
[7]F. Mehran, S. E. Barnes, T. R. McGuire, T. R Dinger, D. L. Kaiser, and F. Holtzberg, Solid State Commun. **66**, 299 (1988).
[8]C. P. Enz, Z. Phys. B **80**, 317 (1990).
[9]F. Mehran, S. E. Barnes, G. V. Chandrashekhar, T. R. McGuire, and M. W. Shafer, Solid State Commun. **67**, 1187 (1988).
[10]S. A. Kivelson, D. S. Rokhsar, and J. P. Sethna, Phys. Rev. B **35**, 8865 (1987).
[11]K. W. H. Stevens, Czech. J. Phys. **41**, 819 (1991).
[12]S. Chakravarty and R. Orbach, Phys. Rev. Lett. **64**, 224 (1990).
[13]A. V. Lazuta, Physica C **181**, 127 (1991).
[14]R. Janes, K. K. Singh, S. D. Burnside, and P. P. Edwards, Solid State Commun. **79**, 241 (1991).
[15]S. Ikegawa, T. Yamashita, T. Sakurai, R. Itti, H. Yamachi, and T. Tanaka, Phys. Rev. B **43**, 2885 (1991).
[16]T. Miyatake, K. Yamaguchi, T. Takata, N. Koshizuka, and S. Tanaka, Phys. Rev. B **44**, 10 139 (1991).
[17]K. Kindo, M. Honda, T. Kohashi, and M. Date, J. Phys. Soc. Jpn. **59**, 2332 (1990).
[18]V. Kalmeyer and R. B. Laughlin, Phys. Rev. Lett. **59**, 2095 (1987).
[19]B. I. Halperin, J. March-Russel, and F. Wilczek, Phys. Rev. B **40**, 8726 (1989).
[20]X. G. Wen, F. Wilczek, and A. Zee, Phys. Rev. B **39**, 11 413 (1989).
[21]F. Wilczek, *Fractional Statistics and Anyon Superconductivity* (World Scientific, Singapore, 1990).
[22]I. Dzialoshinski, A. Polyakov, and P. Wiegmann, Phys. Lett. **127**, 112 (1988).
[23]A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970).
[24]Y. Ajiro, S. A. Friedberg, and S. A. Vander Ven, Phys. Rev. B **12**, 39 (1975).
[25]W. M. Walsh, Jr., Phys. Rev. **114**, 1473 (1959).
[26]R. S. Rubins and T. D. Black, Chem. Phys. Lett. **81**, 450 (1981).
[27]K. B. Lyons, J. Kwo, J. F. Dillon, Jr., G. P. Espinosa, M. McGlashan-Powell, A. P. Ramirez, and L. F. Schneemeyer, Phys. Rev. Lett. **64**, 2949 (1990).
[28]T. W. Lawrence, A. Szöke, and R. B. Laughlin (unpublished).