Formation of localized magnetic moments in zinc-doped lanthanum–strontium superconductors

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ESR studies of $La_{1.82}Sr_{0.18}(Cu_{1-x}Zn_x)O_4$ show that replacement of the copper ions by nonmagnetic zinc ions leads to the formation of complexes with localized magnetic moments. At zinc concentrations of ~ 1 at. % the number of magnetic moments is close to the number of replaced ions. This result is important for verification of microscopic models of high-temperature superconductors.

1. Of the well-known results on the effect of replacement of the copper ions by ions of other elements the most impressive is the suppression of superconductivity by zinc or gallium doping, for which a concentration of 2–3 at. % of the dopants is sufficient.[1-3] This result is surprising, because these ions in metals have a $3d^{10}$ configuration, i.e., they are nonmagnetic. For ordinary superconductors the effect of this type of impurity on the transition temperature is insignificant. Consequently, suppression of T_c by Zn or Ga doping can be considered as an effect which reflects the particular nature of high-temperature superconductors. It would seem that replacement of the Cu^{2+} ions is a method by which the electronic correlations could be studied directly, since the spins are excluded from the spin sublattice. To determine the changes arising in the electron system, magnetic measurement data are required. With this in mind, we have carried out ESR studies of $La_{1.82}Sr_{0.18}(Cu_{1-x}Zn_x)O_4$, replacing part of the copper by zinc (see also Ref. 4).

2. The measurements were carried out using a Bruker BER-418S spectrometer at a frequency of 9.4 GHz. The investigated samples consisted of powders oriented by a magnetic field, with mean size of the crystallites ~ 5 μm, embedded in paraffin. The magnitude of the magnetic field used to orient the crystallites was ~ 10 kG. The magnetic field orients the crystallites in such a way that the CuO_2 plane is aligned perpendicular to it. The degree of orientation of the basis planes was no less than 90%.

In the samples of $La_{1.82}Sr_{0.18}CuO_4$ without Zn impurity, ESR was not observed at any temperature in the range from 6 K to 36 K, in agreement with Ref. 5. Beginning with a zinc concentration of 0.5 at. %, we were able to observe the ESR line.[1)] Figure 1 shows the ESR data for zinc concentrations of 1 at. % and 3 at. %. Figures 1a and 1b are plots of the resonant field and the total line intensity as functions of the temperature, with the magnetic field perpendicular to the CuO_2 plane. The anomalies at $T \approx 150$ K for 3 at. % and respectively at $T \approx 80$ K for 1 at. % are reminiscent of the anomalies that usually arise in the realignment of spin systems. Interesting data on the angular dependences of the g-factor are shown in Fig. 1c. The strong anisotropy of the g-factor accounts for the fact that there is no resonance in unoriented powders. Taking

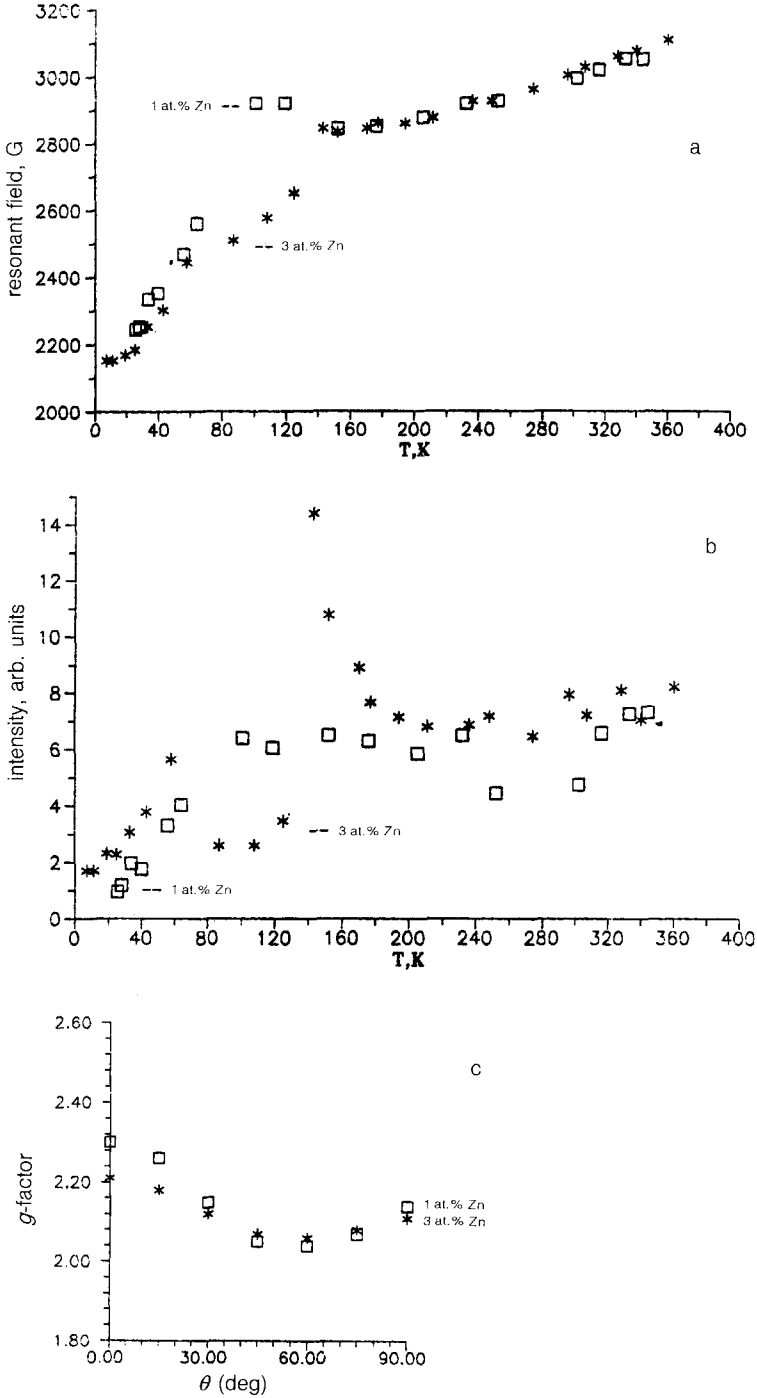

FIG. 1. Dependence of the resonant field (in Gauss) (a) and the total line intensity (b) on temperature (□—1 at. % Zn, *—3 at. % Zn), and of the g-factor on $\theta(c)$. θ is the inclination angle of the magnetic field with respect to the normal to the CuO_2 basis plane.

the total intensity of the resonance line to be proportional to the magnetic susceptibility of the localized spins and assuming that their number coincides with the number of zinc ions, we find that their effective magnetic moment is close to $\sqrt{3}\mu_B$—the nominal value for Cu^{2+} ions: for 1 at. % it is $1.6\mu_B$ and for 3 at. % it is $1.5\mu_B$. For 5 at. % the moment is much smaller. In other words, at this concentration the action of the dopants can no longer be considered as independent.

3. The deviation of the g-factor from the value $g = 2$ is due to the unfreezing of the orbital motion[6] and depends on the spin-orbit value. Therefore, localization of the magnetic moments at the oxygen atoms is excluded by the small magnitude of the spin-orbit interaction, which cannot account for the observed order of magnitude of Δg. The possibility that magnetic moments are formed directly on the zinc ions has a low probability due to the spherical symmetry of these ions. As the copper ions located in the crystal field of the prolate oxygen octahedron, the behavior of $\Delta g(\theta)$ obtained for them is intrinsic. The splitting of the $3d$ level by the crystal field leads to the result that for an isolated Cu^{2+} ion the ground state had $3d_{x^2-y^2}$ symmetry, but the correction to the g-factor due to the spin-orbit coupling is $\Delta g = \Delta g_\perp (1 + 3\cos^2\theta)$. For the copper ions the spin-orbit coupling constant is $\sim 10^3$ K, but the magnitude of the level splitting due to the crystal field is ~ 1 eV. Therefore, the copper ions can provide the observed order of magnitude, $\Delta g \sim 0.1$. Of course, a consideration based on isolated copper ions can only give an indication of what is going on. In reality the mixing of wave functions leads to a more complicated angular dependence of $\Delta g(\theta)$.

Thus, on the basis of the data on the deviation of the g-factor, its angular dependence, and an analysis of the effective magnetic moment, we conclude that zinc doping leads to the formation of a complex which is associated with it, whose localized magnetic moment is located on the copper ion. This conclusion correlates with the measurements of the static susceptibility χ and the resistance ρ. It was shown in Ref. 3 that at low T the susceptibility χ obeys the Curie–Weiss law. In addition, their analysis of the behavior of ρ allowed the authors of Ref. 3 to suggest the existence of a Kondo effect. Our measurements of χ and ρ, in general, agree with these results. We note that the magnitude of the effective magnetic moment, which was extracted from direct measurements of the susceptibility, at a concentration of 1 at. % in our case is $1.3\,\mu_B$.

4. We will now explain why, in our opinion, one should expect the appearance of localized magnetic moments in such systems. It is well known,[7–10] that the problem of a strongly correlated electronic liquid is close to the compact electrodynamics in $(2 + 1)$-measurements.[11] Therefore, the interaction of the defects in such systems grows with distance at least logarithmically, and in the case of confinement[11] even linearly. Interactions of such kind are usually described by strings which connect the defects. If the distance between the defects is sufficiently large, the energy of the system can be lowered by breaking the string with the formation of a pair of spin excitations (see Fig. 2). As a result, each dopant forms a complex which has a localized magnetic moment.

Let us discuss this situation in the context of some concrete models. One such model is the theory of dimers (resonant valence bonds on neighboring sites).[12] Dissociation of the dimers, which is accompanied by the formation of two spinons, requires the expenditure of considerable energy. In addition to the resonance between the

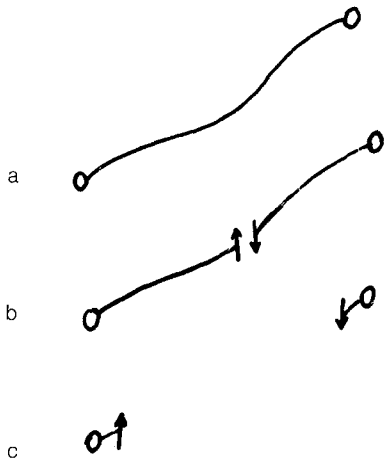

FIG. 2. Diagram of the formation of localized moments. O—Defect (zinc ion): →—an excitation which carries spin (a spinon): a) interaction of the defects described by a string; b) breaking of the string due to creation of a spinon pair; c) shortening of the string segments with the formation of a dopant—spinon pair.

bonds, the quantum fluctuations allow the spinons and the holons—sites which are not occupied by electrons—to move. In this theory it is important that the quadratic lattices have two topologically different types of holons which are situated at the "red" or "black" sublattice of the original lattice (this also applies to the spinons). If the interaction energy of the dopants is sufficient for the dimers to dissociate, dopant–spinon complexes will form. Each of these complexes is comprised of objects of different color. The theory of dimers has been applied[13–15] to the description of superconductivity in terms of holon pairs. The destruction of such superconductivity by a spinon-dopant complex occurs as a result of the possibility of the virtual exchange of color between the holon and the spinon of the superconducting pair. This is completely analogous with the suppression of ordinary superconductivity by magnetic impurities,[16] with the one difference that the role of spin here is played by color.

Another widely used model[9,17,18] assumes that the spins are correlated antiferromagnetically inside a radius r_c. The spin variables are described in this theory by Z-quanta. The mechanism for the formation of complexes which link the Z-quanta is close to the one considered here and is described in Ref. 18. However, the observation of ESR on localized Z-quanta is unlikely. The point is that ESR requires the presence of a Kramers doublet. In antiferromagnets time-inversion symmetry is connected with translational symmetry, but the presence of a defect breaks the translational symmetry. Therefore, if a complex with a bound magnetic moment is localized in a region of dimension r_c, then the observation of ESR is impossible. On the other hand, a dopant concentration on the order of 1 at. % is too high for the formation of bound complexes with dimensions appreciably higher than r_c. It is thus difficult to reconcile this model with the observation of ESR. Here it is appropriate to point out that measurements of the antiferromagnet $La_2(Cu_{1-x}Zn_x)O_4$ failed to detect a paramagnetic resonance associated with zinc doping.

In conclusion we note the following circumstance. Dynamic holes screen the interaction of the defects, thereby suppressing the creation of spinons. It is possible, therefore, that the explanation of the effect requires going beyond the scope of the models discussed here and that this pursuit may be a test of the microscopic theories of high-temperature superconductors.

[1)] In the presence of excess oxygen, a resonance is not observed in the zinc-doped samples, although this has no effect on the suppression of T_c. It is possible that excess oxygen leads to effective spin relaxation.

[1]Gang Xiao *et al.*, Phys. Rev. Lett. **60**, 1446 (1988).
[2]Gang Xiao *et al.*, Phys. Rev. B **39**, 315 (1989).
[3]M. Z. Cieplak *et al.*, Phys. B **39**, 4222 (1989).
[4]A. M. Finkel'stein *et al.*, USA-USSR Conference on Frontiers in Condensed Matter Theory, December 1989, New York.
[5]H. Maletta *et al.*, Jpn. J. Appl. Phys. **26**, 1143 (1987); F. Mehran and P. W. Anderson, Solid State Commun. **71**, 29 (1989).
[6]A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford (1970).
[7]G. Baskaran and P. W. Anderson, Phys. Rev. B **37**, 580 (1988).
[8]A. Nakamuro and T. Matsui, Phys. Rev. B **37**, 7940 (1988).
[9]P. B. Wiegmann, Phys. Rev. Lett. **60**, 821 (1988).
[10]N. Read and S. Sachdev, Phys. Rev. Lett. **62**, 1694 (1989).
[11]A. M. Polyakov, Nucl. Phys. B **120**, 429 (1977).
[12]S. Kivelson *et al.*, Phys. Rev. B **35**, 8865 (1987).
[13]D. S. Rokhsar and S. Kivelson, Phys. Rev. Lett. **61**, 2376 (1988).
[14]L. B. Ioffe and A. I. Larkin, Preprint NSF-ITP-89-59.
[15]E. Fradkin and S. Kivelson, Preprint, 1989.
[16]A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1960) [Sov. Phys. JETP **12**, 1243 (1960)].
[17]X. G. Wen, Phys. Rev. B **39**, 7223 (1989).
[18]P. A. Lee, Phys. Rev. Lett. **63**, 680 (1988).

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