JOURNAL OF SOLID STATE CHEMISTRY 111, 2–3 (1994)

Metal–Insulator Transition in Copper Oxide Superconductors

Nevill Mott

IRC for Superconductivity, University of Cambridge, Cambridge CB3 DME, United Kingdom

Received July 8, 1993; accepted January 13, 1994
IN HONOR OF C. N. R. RAO ON HIS 60TH BIRTHDAY

The metal–insulator transition in a copper-oxide superconductor is discussed. It is shown that at the composition where this occurs at zero temperatures, the number of carriers (bipolarons) varies at T. This gives a tentative explanation of the behavior of the Hall coefficient. Professor Rao's work has shown that there are important correlations between T_c and hole concentration in a range of cuprate superconductors based on lanthanum, neodymium, thallium, and bismuth. This paper discusses the semiconductor–superconductor transition for these materials. © 1994 Academic Press, Inc.

Professor Rao (1) has shown that there are important correlations between T_c and hole concentration in a range of cuprate superconductors based on lanthanum, neodymium, thallium, and bismuth. This paper discusses the semiconductor–superconductor transition for these materials. All of them start with similar behavior. Starting with an antiferromagnetic insulator, the material is doped, normally with an acceptor. The first result is that the Néel temperature drops to zero; in $La_{2-x}Sr_xCuO_4$ this occurs at $x = 0.03$, though in the n-type materials the drop is much slower. There is then a range of nonmetallic (spin glass?) behavior, where conduction is by some kind of hopping. There is finally a transition to metallic (superconducting) behavior, with a low T_c which rises rapidly.

We have first to ask why doping destroys the antiferromagnetic order in an antiferromagnetic semiconductor, such as $Gd_{3-x}V_xS_4$ (V stands for vacancy). The carriers in the conduction band form spin polarons (ferrons). The concept of this entity was introduced by de Gennes (2) in 1961 and is illustrated in Fig. 1; the cluster of spins greatly increases the mass of the carriers, and in the above material they are subject to Anderson localization, but are destroyed by a magnetic field (3). I supposed that they were formed in, for instance, $La_{2-x}Sr_xCuO_4$, but work with polarized neutrons showed that they carry no magnetic moment. I therefore assumed (4) that energy is lowered if the configuration is changed to that (in 2D) of a metallic disc, highly correlated in the sense of Brinkman and Rice (5); most of the energy needed to break down the strong AF correlations would then be avoided.

The radius R of the spin polaron is thought to be of order $a(t/J)^{1/5}$, where t is the energy transfer integral for a carrier (an oxygen 2p hole) and J the AF coupling constant. According to Maekawa *et al.* (6) (see also Lu and Si (7)) t/J should be large enough for all copper sites to be included within such a polaron, thus destroying the AF order.

It is perhaps noteworthy that for the n-type material, T_c does not drop so rapidly with doping. Here the carrier forms a $Cu3d^{10}$ state, and t should be much smaller, so we can assume that more of our spin polarons are needed (see Zhang and Bennemann (8)). The absence of the apical oxygen for an n-type material will also affect the band structure, and may be relevant to the different form of the spin polaron.

Thomas (9) and Armstrong and Edwards (10) have supposed that the transition to a metallic state occurs at a concentration given by the empirical formula

$$n^{1/3}a_H = 0.26. \qquad [1]$$

To check this, one needs to estimate a_H, which Thomas takes to be from 3 to 5 Å. Mott (11) finds that Eq. [1], with a slightly different constant, can be deduced from the overlapping of two Hubbard bands, or alternatively as an Anderson transition for noninteracting particles. We think an Anderson (second order) transition is occurring here. The carriers are dielectric polarons, with spin polarons only forming a core. The dielectric effect must be responsible for much of the mass enhancement, since these lightly doped materials show a large isotope effect.

As soon as the carriers become free to move, we suppose they form bosons. The critical temperature is that at which the boson gas become degenerate. Neglecting interaction, this gives in three dimensions

$$k_B T_c = 3.3\, n^{2/3}\hbar^2/m,$$

0022-4596/94 $6.00

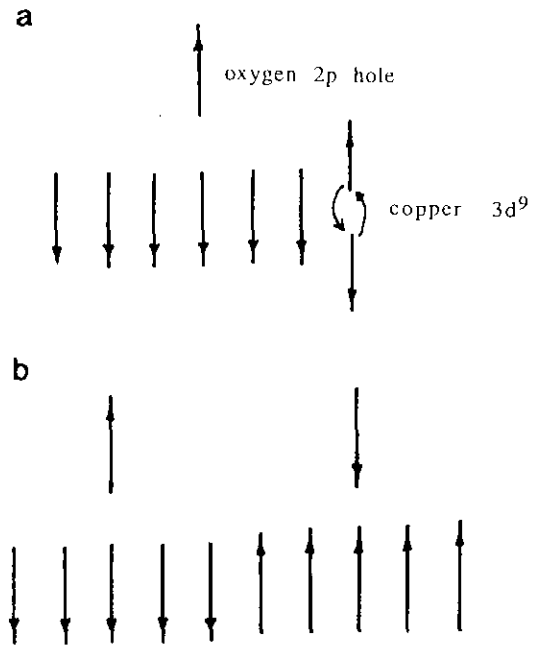

FIG. 1. (a) Spin polaron, and (b) spin bipolaron.

where

$$m = (m_1 m_2 m_3)^{1/3}$$

and m_1, etc., are the boson effective masses in three crystallographic directions. As is well known, in two dimensions, no Bose condensation is possible, but with interaction this is not so.

In general, it appears from the study of He that interactions do not have a major effect on T_c (Mott (12)).

Striking evidence that the transition from semiconductor to superconductor is of Anderson type comes from a study of the Hall effect, which for low values of the doping above T_c behaves like

$$R_H \propto 1/T.$$

This suggests that the number of carriers behaves like T. This differs slightly from what we should expect for an Anderson transition. At zero temperature the conductivity should be of the form (in a three-dimensional system)

$$\sigma = \sigma_{min}\left[1 - \frac{1}{(klg)^2}\right], \qquad [2]$$

where both g and l vary with this energy. At a finite temperature (Mott and Kaveh (13), Mott (11))

$$\sigma = \sigma_{min}\left[1 - \frac{1}{(klg)^2}\left\{1 - \frac{a}{K}\right\}\right], \qquad [3]$$

and since at $T = 0$ the conductivity vanishes, $klg = 1$ and at finite temperatures

$$\sigma = \sigma_{min} a/L.$$

Here L is the inelastic diffusion length given by

$$L = \sqrt{D\tau}.$$

We suppose that D is independent of temperature, and τ, determined by Landau Baber scattering, is proportional to $1/T^2$. Thus

$$L = 1/T,$$

and the conductivity varies as T.

This peculiar behavior applies only at the composition for the transition; in general σ is $n\tau$, which is proportional to $1/T$.

Investigations by Thomas *et al.* (14) on SiP using stress tuning show that in the limit of low T σ for the concentration and stress at the $T = 0$ transition varies as $T^{1/2}$ (see also Milligan, (15)).

The square root comes from the correction to Eq. [3] resulting from interactions (Altshuler and Aronov (16). We assume that this is absent, because the correction arises from a change in the density of state near the Fermi energy, and in our case the density of states comes from Bosons.

REFERENCES

1. C. N. R. Rao, *Philos. Trans. R. Soc. Ser. A* **356,** 595 (1991); and *in* "Chemistry of Low Temperature Superconductors" (C. N. R. Rao, Ed), p. 87. World Scientific, Singapore (1991).
2. P. G. de Gennes, *J. Phys. Radium* **23,** 630 (1962).
3. S. Penney, D. Von Molnar, F. Kaiser, F. Holtsberg, and A. W. Kleinsasser, *Phys. Rev. B* **38,** 2918 (1988).
4. N. F. Mott, *Physica C* **295,** 191 (1993).
5. W. F. Brinkman, and T. M. Rice, *Phys. Rev. B* **7,** 1568 (1973).
6. S. Maekawa, Inonev, and M. Miyazatu, *in* "Mechanism of High Temperature Superconductors" (H. Kamimura and A. Oshiyama, Eds.), p. 68. Materials Science, Vol. 11, Springer-Verlag, Berlin/New York (1991).
7. J. P. Lu and Q. Si, *Phys. Rev. B* **42,** 950 (1990).
8. W. Zang and K. H. Bennemann, *Phys. Rev. B* **45,** 487 (1992).
9. G. A. Thomas *in* "High Temperature Superconductivity" (D. P. Tunstall and W. Barford, Eds.), p. 145. SUSS in Physics (1991).
10. A. R. Armstrong and P. P. Edwards, "Chemistry of Superconducting Oxides," p. 259. Annual Report C, R. Soc. Chemistry (1991).
11. N. F. Mott, "Metal–Insulator Transitions," 2nd ed. Taylor & Francis, London (1991).
12. N. F. Mott, *J. Phys. Condensed Matter* **5,** 3487 (1993).
13. N. F. Mott, and M. Kaveh, *Adv. Phys.* **34,** 329 (1985).
14. G. A. Thomas, M. A. Paulanen, and T. F. Rosenbaum, *Phys. Rev. B* **27,** 2897 (1983).
15. R. F. Milligan *in* "The Metallic and Non-metallic States of Matter" (P. P. Edwards and C. N. R. Rao, Eds.), p. 169. Taylor & Francis, London (1985).
16. B. L. Altshular and A. G. Aronov, *Solid State Commun.* **36,** 115 (1979).