Electronic properties of $Sr_{14}Cu_{24}O_{41}$

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Crystals of orthorhombic $Sr_{14}Cu_{24}O_{41}$ are semiconducting, with an activation energy of 0.18(2) eV for conduction along c, the direction lying parallel to both the (Cu_2O_3) planes and the (CuO_2) chains. The magnetic susceptibility above 80 K follows a Curie-Weiss law with $\Theta = -95$ K and $p_{eff} = 0.65\mu_B/Cu$ in the ac plane and $\Theta = -190$ and $p_{eff} = 0.94\mu_B/Cu$ along b, the direction perpendicular to the (Cu_2O_3) planes and the (CuO_2) chains. There is an indication of antiferromagnetic order below $T_N = 60$ K, and a Curie contribution at low temperature due to localized free spins [0.4(1) with $S = \frac{1}{2}$ per formula]. The specific heat measured in the range 2–12 K is of the form $AT^{-2} + \gamma T + \beta T^3$, where $A = 1080$ mJ K/mole, $\gamma = 100$ mJ/mole K^2, and $\beta = 5.93$ mJ/mole K^3. A 5-T magnetic field greatly enhances the low-temperature specific heat, an effect which is attributed to the localized states with $S = \frac{1}{2}$. The linear term is attributed to a localized density of states with no net spin, possibly associated with peroxide ions. The relevance of these results to the low-temperature specific heat of copper-oxide superconductors is discussed.

INTRODUCTION

Many high-temperature copper oxide superconductors have a number of common features. A question to resolve experimentally is which of these are intrinsically related to the appearance of the superconducting state. These features include the following.

(i) Chemical compositions which indicate the presence of holes relative to the normal ionic configurations $Cu^{2+}(3d^9)$ and $O^{2-}(2p^6)$. It is now established that these holes reside principally in bands derived from $O(2p)$ orbitals.[1,2]

(ii) Structures that include infinite (CuO_2) planes where copper is a square-planar oxygen coordination.[3]

(iii) A resistivity in the normal state that is metallic in the plane, but shows an unusually large linear variation with temperature.[4,5]

(iv) A low-temperature specific heat in the superconducting state that includes a large term linear in temperature. The coefficient γ is typically 5 mJ/mole K^2 per Cu.[6]

Systematic studies of the crystal chemistry have established that superconductivity is associated with stacks of n square-planar (CuO_2) layers interspersed with $n-1$ layers of large, usually divalent cations.[3] The superconducting transition temperature T_c is found to increase with n, at least up to $n = 4$ in the Tl-Sr-Ca-Cu oxide series, so there is naturally an interest in the electronic properties of the $n = \infty$ end member, $M^{2+}CuO_2$ and related compounds. Siegrist *et al.*[7] recently synthesized $(Ca_{0.86}Sr_{0.14})CuO_2$; that material is naturally semiconducting, as the formula indicates normal divalent configurations for copper and oxygen. No holes are present.

Recently, a number of groups have encountered elongated flat crystals of approximate composition MCu_2O_3, while attempting to grow superconductors in the Bi-Sr-Ca-Cu oxide series.[8–13] A new orthorhombic structure type $M_{14}Cu_{24}O_{41}$ has been identified, where M can be an alkaline-earth cation,[8–11] a mixture of alkaline earths, rare earths, or bismuth,[12] or even a mixture of al-

kaline earths and copper.[13] The composition indicates that there are six holes per formula when M is a divalent cation. Furthermore, this structure includes both Cu-O planes and chains, and the copper in both structural elements is at the center of squares of oxygen lying parallel to the ac plane. However, the structures of the (Cu_2O_3) planes and the (CuO_2) chains are not commensurate; a superstructure of the basic orthorhombic cell ($a = 11.3$ Å, $b = 13.0$ Å, $c = 3.9$ Å) with $c' = 7c$ includes almost, but not exactly ten repeat units of the chains.[9] A general view of the structure is presented in Fig. 1. The (Cu_2O_3) planes of $M_{14}Cu_{24}O_{41}$ differ from the corner-sharing (CuO_2) planes of the high-T_c superconductors in that some extra squares are filling in $M_{14}Cu_{24}O_{41}$, giving a pattern of edge- and corner-sharing CuO_4 squares.

Here we report on the electrical conductivity, magnetic susceptibility, and heat capacity of $Sr_{14}Cu_{24}O_{41}$, and compare the results with those of high-T_c copper oxide superconductors.

RESULTS

Crystals of $Sr_{14}Cu_{24}O_{41}$ were prepared as described in Ref. 10. They had the form of thin plates or laths, with the long axis parallel to c. Lattice parameters were $a = 11.45$ Å, $b = 13.35$ Å, $c = 3.987$ Å.

The temperature dependence of the resistivity measured by the four-probe method on a bar $0.1 \times 0.1 \times 5$ mm^3 is shown in Fig. 2. The crystal is semiconducting along c (presumably the direction of highest conductivity) and an activation energy of 0.18(2) eV is deduced in the temperature range 125–300 K.

Magnetic susceptibility was measured on a superconducting quantum interference device magnetometer with the field approximately parallel to each of the three crystallographic directions. Data are shown in Fig. 3 where it can be seen that the susceptibility measured in the ac plane differs substantially from that measured perpendic-
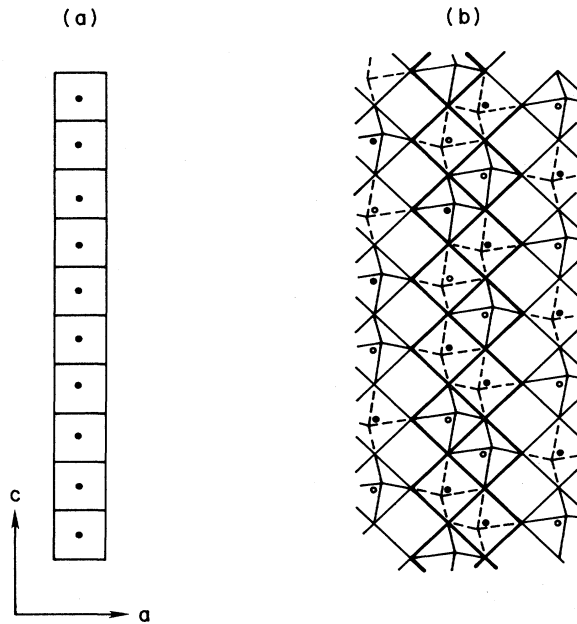
(a)   (b)

FIG. 1. Structures of the alternating copper-containing layers in $Sr_{14}Cu_{24}O_{41}$ (viewed along b): (a) (CuO_2) chain with distorted square-planar coordination of copper (filled circles): (b) (Cu_2O_3) plane, showing a ribbon of edge-sharing Cu-O pyramids pointing above and below the plane of the paper (heavily outlined) and it links to neighboring ribbons. A possible antiferromagnetic arrangement is indicated by open and filled circles for copper atoms.

ular to this plane. In all three directions there is typical Curie-Weiss behavior $\chi = C/(T - \Theta)$ above 80 K, with values of $\Theta = -95$ K and $C = 1.9$ per mole Cu with the field parallel to a and c, and values of $\Theta = -190$ K and $C = 1.7$ per mole Cu with the field parallel to b. The corresponding values of p_{eff} per copper are $0.65\mu_B$ and $0.94\mu_B$, respectively; the value expected for $S = \frac{1}{2}$ is $1.73\mu_B$. The low value of the moment may reflect strong mixing of the Cu $3d_{x^2-y^2}$ orbitals with $2p$ orbitals on the
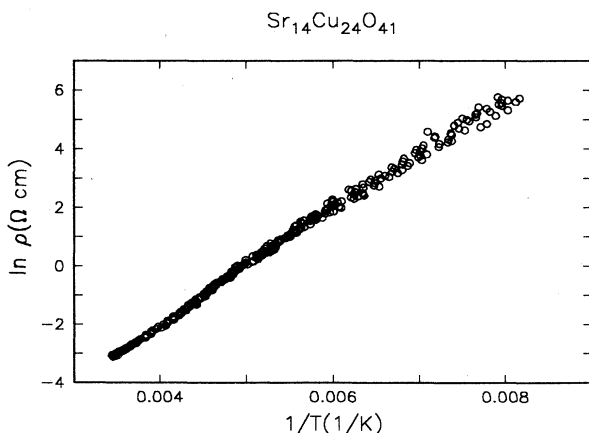

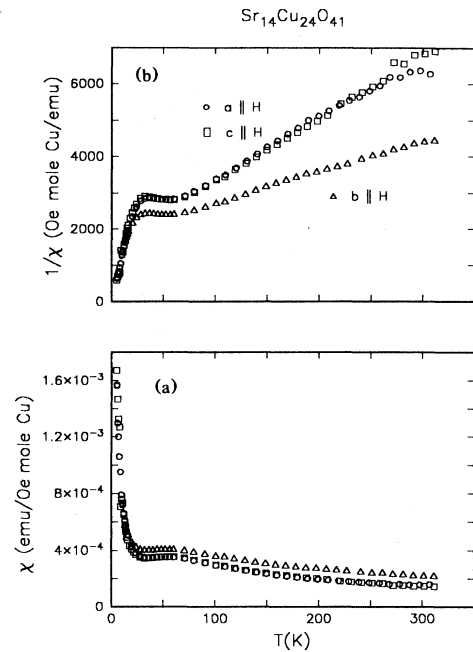FIG. 2. Temperature dependence of the resistivity of a single crystal of $Sr_{14}Cu_{24}O_{41}$ (measured along c).

FIG. 3. (a) Magnetic susceptibility and (b) inverse susceptibility of $Sr_{14}Cu_{24}O_{41}$, measured parallel to each of the crystallographic directions.

surrounding oxygen sites. The susceptibility passes through a broad maximum at 60 K which suggests that antiferromagnetic order is established there. Below 40 K, it rises again, the additional susceptibility following a Curie law $\chi = C/T$; its magnitude corresponding to 0.4(1) "impurities" with $S = \frac{1}{2}$ per formula. There is no hysteresis and no ferromagnetic component in the magnetization curves at 2 K, suggesting that this upturn is due to an increase in susceptibility, rather than to the appearance of a weak ferromagnetic moment due to spin canting, as in La_2CuO_4.[14]

The specific heat was measured in the range 2–12 K, on a sample composed of the same four crystals (total mass 3.8 mg) that were used for susceptibility measurements. Data were collected using the thermal relaxation method[15] with and without an applied field of 5 T. Results are plotted in Fig. 4 as C/T vs T^2. In zero field, the data follow a straight line with an upturn below 4 K. A substantial increase in heat capacity is observed throughout the range when the field is applied. Least-squares fitting to the expression $AT^{-2} + \gamma T + \beta T^3$ yields, in zero field, $A = 1080$ mJ K/mole, $\gamma = 100$ mJ/mole K^2, and $\beta = 5.93$ mJ/mole K^3, where the numbers refer to a mole of $Sr_{14}Cu_{24}O_{41}$. The first term is a way of fitting the tail of the Schottky anomaly due to some sort of magnetic centers having a zero-field splitting less than about 2 K. The second term can, in principle, be magnetic or electronic in nature, and it is discussed further in the next section. The third term arises essentially from long-wavelength lattice vibrations. Ignoring a possible contribution from antiferromagnetic spin waves, we find a Debye temperature of 296 K.

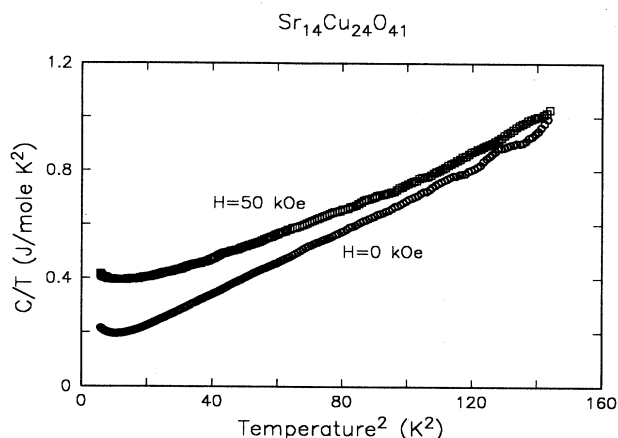The data in an applied field allow us to estimate the

$Sr_{14}Cu_{24}O_{41}$

FIG. 4. Specific heat of $Sr_{14}Cu_{24}O_{41}$, plotted as C/T vs T^2.

number of impurities that are responsible for the low-temperature upturn in heat capacity. Assuming they have $S = \frac{1}{2}$, the difference in the 5 and 0 T curves was fitted to a Schottky function $s(\delta/T)$ yielding the impurity concentration 0.28(6) per formula unit and the splitting $\delta = 12(2)$ K. The splitting needed to explain the upturn in zero applied field is 1.2 K. The impurity concentration is consistent with experimental error with that estimated from the Curie upturn in the low-temperature susceptibility.

DISCUSSION

The first question of interest is why $Sr_{14}Cu_{24}O_{41}$ is not a superconductor. From the composition, the number of holes is six, which corresponds to 0.25 holes per copper, a number that is close to the value for copper in the (CuO_2) planes of $(La_{1-x}M_x)_2CuO_4$ (Ref. 16) and $YBa_2Cu_3O_{7-\delta}$ (Ref. 17) to maximize T_c. Furthermore, the planes in $Sr_{14}Cu_{24}O_{41}$ provide distorted Jahn-Teller sites for copper (square pyramids with an elongated vertical Cu-O bond), just as in the known copper-oxide superconductors. We do not know whether the holes are located in (Cu_2O_3) planes or (CuO_2) chains, although charge balance may favor the latter. In any case, there is an evident structural difference between $Sr_{14}Cu_{24}O_{41}$ and $(La_{1-x}M_x)_2CuO_4$, $YBa_2Cu_3O_{7-\delta}$, or $Bi_2Sr_2CaCu_2O_8$, for example. In the former, both the oxygen squares in the (CuO_2) chains and the oxygen pyramids in the (Cu_2O_3) planes share edges in addition to corners. Admitting that the 180° Cu−O−Cu superexchange bonds provide the dominant antiferromagnetic interaction, the (Cu_2O_3) planes will tend to divide up into decoupled "ladders," infinite strips just two copper atoms wide parallel to the c axis, as schematized in Fig. 1(b). The spin-correlated valence-bond liquid state[18] that might result from this will have quasi-one-dimensional rather than two-dimensional character.

The antiferromagnetic character of $Sr_{14}Cu_{24}O_{41}$ may be compared with copper oxides with few mobile holes in the (CuO_2) planes, such as $(La_{1-x}M_x)_2CuO_4$ with $x < 0.05$ or $YBa_2Cu_3O_{7-\delta}$ with $\delta > 0.4$. In $Sr_{14}Cu_{24}O_{41}$,

the average exchange integral deduced from an average $\Theta = 127$ K is $J = 145$ K. This is arrived at by counting only three strong 180° Cu−O−Cu superexchange bonds per copper for each of the 14 copper atoms in the (Cu_2O_3) planes and no such bonds for the 10 copper atoms in the (CuO_2) chains, resulting in $(14 \times 3 + 10 \times 0)/24 = 1.75$ strong bonds per copper atom. This J value is much lower than the value of 1300 K derived for the superexchange interaction in $YBa_2Cu_3O_{7-\delta}$,[19] probably because of competing ferromagnetic exchange paths in $Sr_{14}Cu_{24}O_{41}$.

Since there is ideally no net interaction between adjacent ladders, the coupling must be provided by defects, or via the chains by either direct Cu-Cu overlap or 90° Cu-O-Cu superexchange. As the chains and planes are strictly incommensurate, defects could again play a part. It is likely that the antiferromagnetic structure is modulated somehow along the c direction,[20] but a neutron study of the magnetic structure is needed to determine this. The small number of free spins may be associated with Cu^{2+} or O^- ions at points in the structure where interactions with the antiferromagnetically aligned neighbors cancel exactly.

In some respects the most interesting feature of our data is the large linear term in the low-temperature specific heat, which is remarkably similar to that found in many copper oxide superconductors.[6] The magnitude (5 mJ/mole K^2 per Cu) is practically the same as that found in crystals of $YBa_2Cu_3O_{7-\delta}$ (Ref. 21) and $Bi_2Sr_2-CaCu_2O_8$.[22] Since $Sr_{14}Cu_{24}O_{41}$ is a semiconductor with electrons that are localized at low temperatures, it would appear that there is no direct connection between the linear term and superconductivity. Studies of the temperature dependence of the penetration depth in $YBa_2Cu_3O_{7-\delta}$ have led to the conclusion that a gap exists around the entire Fermi surface.[23,24] Where, then, is the linear specific heat coming from?

A plausible explanation in oxides is to associate it with a density of localized electronic states. This has been well documented by Chakraverty, Sienko, and Bonnerst[25] in their work on the vanadium bronzes. The localized states in the present materials are probably O(2p) holes. Their density (assuming no oxygen deficit with respect to the $Sr_{14}Cu_{24}O_{41}$ formula) is 6×10^{21} cm^{-3}. Most of these localized holes have their spins paired; only about 10% of them respond to the applied field in susceptibility or specific heat. They may be exchange coupled to the antiferromagnetic structure or to each other, with the latter case seeming more likely as it can occur in either superconductors or semiconductors. Two coupled O(2p) holes form a peroxide ion O_2^{2-}. Localized rearrangements of these ions on the oxygen lattice are a possible origin of the low-temperature linear term in the specific heat.

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