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Hall-effect measurements on superconducting and nonsuperconducting copper-oxide-based metals

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The temperature dependence of the Hall effect was studied on single crystals of the layered copper oxide compounds $Bi_2Sr_2CaCu_2O_8$ (2:2:1:2) and $Bi_2Sr_2CuO_6$ (2:2:0:1) with magnetic field perpendicular to and parallel to and parallel to the CuO layers. dc resistivity measurements indicated that the 2:2:1:2 samples have a superconducting transition temperature of 82–84 K; the 2:2:0:1 samples are metallic, but they did not show superconductivity down to 3.0 K. The Hall effect was found to be strongly anisotropic and the interplane electronic transport is determined by electron hopping between the layers. For magnetic fields perpendicular to the layers, the superconducting compound shows a strongly temperature-dependent anomalous increase in the Hall coefficient; the nonsuperconducting material has a much smaller, weakly temperature-dependent Hall effect.

It is generally believed that the high-temperature superconductivity and the large and strongly temperature-dependent Hall coefficient,[1-3] observed in the copper-oxide-based compounds, have a common origin. There have been attempts to prove this conjecture by correlating the critical temperature (T_c) and the Hall effect in doped high-T_c materials.[4-6] However, the nonsuperconducting samples in these studies have a tendency of developing a high-resistance, nonmetallic state at low temperatures. The comparison of a metallic high-T_c compound and a nonmetallic reference compound is not fully conclusive.

In this Rapid Communication we report the results of a comparative study of superconducting and nonsuperconducting single crystals of nominal composition $Bi_2Sr_2CaCu_2O_8$ (hereafter denoted by 2:2:1:2) and $Bi_2Sr_2CuO_6$ (hereafter 2:2:0:1). The transition temperature of the 2:2:1:2 compound was 82 K; the 2:2:0:1 material was metallic (i.e., the resistivity decreased with temperature), but it did not have a superconducting transition down to the lowest temperature measured (3 K). We demonstrate that the large, strongly temperature dependent Hall coefficient is a unique feature of the superconducting sample. The comparison of the Hall-effect measured in different crystallographic directions suggests that this behavior is related to the charge transport in the CuO planes.

The measurements with H parallel to c (cyclotron orbits in the CuO planes) were performed on several thin (1×1 mm$^2\times 3000$ Å) single crystals grown and prepared in our laboratory. The electrical contacts were made of silver epoxy; the contact resistances were less than 1 Ω. A six-probe configuration was used with two current leads and two pairs of Hall-voltage contacts. The signal due to the misalignment of the Hall contacts was eliminated by rotating the sample by 180° at each temperature. Most of the measurements were carried out with 1–2 mA dc in a fixed magnetic field of 7 T; the linearity of the response was also tested at a few selected temperatures. The Hall voltage proved to be proportional to the magnetic field (up to 9 T) and current (up to 10 mA).

For the measurements of the Hall voltage in the c direction (i.e., perpendicular to the CuO planes) we applied both the current and the magnetic field in the ab plane. The typical size of a sample was $2\times 0.3\times 0.05$ mm^3 (the smallest dimension being in the c direction). For the CuO based metals the in-plane resistivity (ρ_{ab}) is much less than the resistivity in the c direction (ρ_c). Side current contacts were used to prevent the "shortening" of the Hall voltage due to the resistivity anisotropy. The Hall effect is also very anisotropic and, therefore, the alignment of the sample in the magnetic field is critical. We took advantage of the extreme anisotropy of the magnetoresistance below T_c, and we oriented the c axis perpendicular to the magnetic field by searching for the minimum in the resistivity in the superconducting state.

The samples were investigated by selected area electron diffraction[7] (Fig. 1). The pseudotetragonal unit-cell dimensions are $a\approx b=5.40\pm 0.05$ for both the 2:2:1:2 and 2:2:0:1 materials.[8] An incommensurate superlattice is apparent for the 2:2:1:2 sample; the b direction is parallel to the superlattice, and the modulation wavelength is $b'=4.7b$, in good quantitative agreement with the published values.[8] The sample is not twinned. The 2:2:0:1 sample has a different superlattice structure; the distinct diffraction patterns of the two specimens allows us to conclude that the 2:2:1:2 sample has no noticeable second phase or inclusions of 2:2:0:1 type and vice versa.

In Fig. 2(a), we present the temperature dependence of the dc resistivity for the 2:2:1:2 and 2:2:0:1 single crystals used in the Hall-effect measurements. The resistance of the 2:2:1:2 sample is linear down to 150 K; the superconducting transition temperature is 82 K (zero resistance). The rounding of the resistivity curve below 110 K is very reproducible and it was observed on crystals obtained from different batches. The 2:2:0:1 sample has a higher room temperature resistivity (650 $\mu\Omega$ cm), and it does not

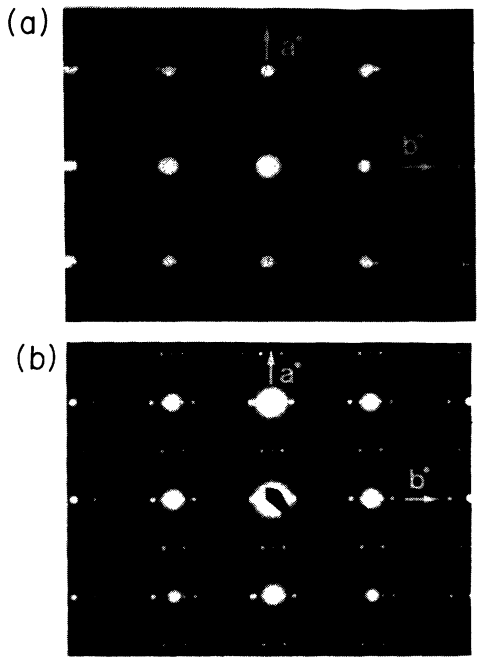

FIG. 1. Electron diffraction pictures obtained for the materials of nominal composition (a) $Bi_2Sr_2CuO_6$ and (b) $Bi_2Sr_2CaCu_2O_8$.

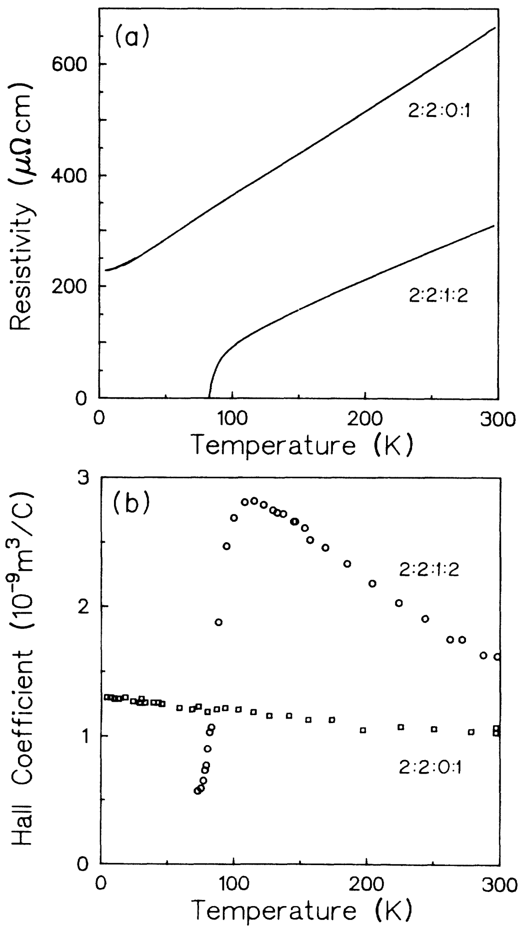

FIG. 2. (a) Temperature dependence of the resistivity and (b) Hall coefficient for the 2:2:0:1 and the 2:2:1:2 samples.

show superconductivity down to 3.0 K. Nevertheless the resistivity is monotonically decreasing with decreasing temperature. There is a finite intercept at zero T ("residual resistivity").

The Hall coefficients (R_H) of the samples are shown in Fig. 2(b). The magnetic field was applied perpendicular to the copper oxide planes. The Hall coefficient of the 2:2:1:2 material agrees well with the results published earlier for this compound[3,9,10] although the temperature dependence is somewhat stronger. Similar R_H vs T was measured on $YBa_2Cu_3O_7$,[1] and on $La_{2-x}Sr_xCuO_4$:[2] R_H increases as the temperature is decreased to 110 K; then it begins to drop as the superconducting transition is approached. The Hall effect is much smaller for the 2:2:0:1 samples and its temperature dependence is weaker. Earlier measurements on polycrystalline samples[11] did not reveal these aspects of the Hall effect.

Figures 3(a) and 3(b) show the Hall-effect data for several samples with the magnetic field applied parallel

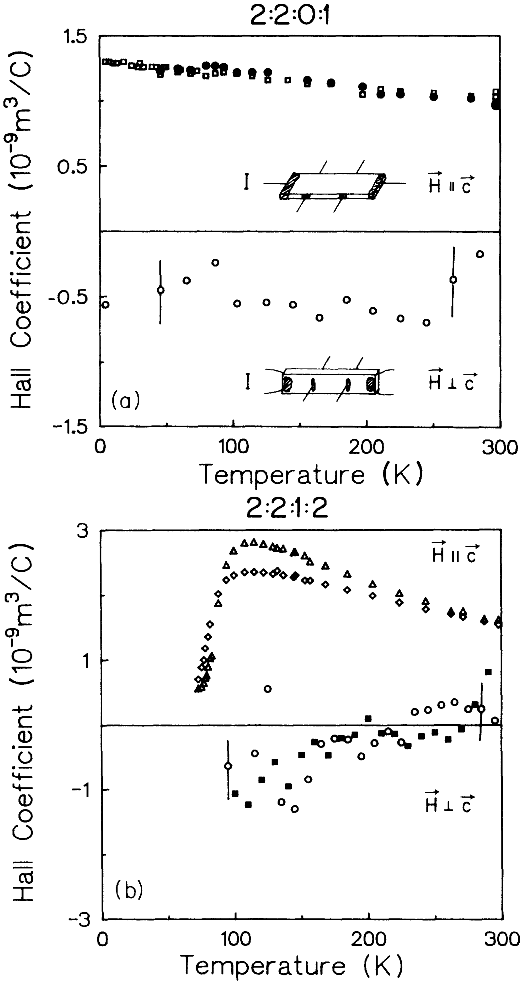

FIG. 3. (a) Temperature dependence of the Hall coefficient of the 2:2:0:1 material for H parallel (solid circles and open squares for two samples) and perpendicular (open circles) to the c direction. The inset shows the contact configuration for the two measurements. (b) Temperature dependence of the Hall coefficient of the 2:2:1:2 material for H parallel (open triangles and diamonds for two samples) and perpendicular (open circles and solid squares for two samples) to the c direction.

and perpendicular to the c axis. Although the errors are relatively large for the perpendicular configuration (i.e., Hall-voltage measured in the c direction), there is no doubt that in this case the Hall effect is weakly temperature dependent and mostly negative for the 2:2:1:2 sample. A negative Hall coefficient was observed in the c direction for $YBa_2Cu_3O_7$ as well.[12,13]

The interpretation of the magnetotransport in the high-temperature superconductors is controversial. One may argue that the strong temperature dependence of the Hall field is due to a delicate, temperature dependent balance between contributions of opposite sign (e.g., electrons and holes, or layers of different type). The universal, material independent nature of the Hall effect makes this interpretation unlikely. Moreover, our results suggest that the correct explanation should account for the anomalous Hall effect and the high-T_c superconductivity simultaneously. Another approach is based on the observation that the high-T_c compounds are close to an antiferromagnetic state. In heavy fermion materials similar behavior was interpreted in terms of skew scattering.[14] The most serious analysis along these lines was presented by Fiory and Grader.[15] The weak point of this approach is the lack of correlation between R_H and magnetic susceptibility χ. In heavy fermion systems R_H and χ have a similar temperature dependence, while in the high-T_c compounds there is an anticorrelation: as T_c is lowered by doping, R_H becomes less temperature dependent[16] and χ develops a Curie-Weiss-type temperature dependence. Also, for skew scattering the Hall coefficient is often field dependent; we do not see evidence for this in the 2:2:1:2 compound.

For magnetic fields perpendicular to the c direction the Hall effect is small, and it has no well-defined positive or negative sign. This, in our opinion, is due to the nonmetallic character of the charge transfer between the CuO planes. A similar situation arises for other low dimensional materials, if the overlap between electronic orbitals is small. For example, the organic compound tetrathiafulvalenium-tetracynoquinodimethanide has a small Hall effect in the direction of lowest conductivity, and the sign of the Hall coefficient is opposite to that of the high conducting direction.[17,18] These observations can be interpreted in terms of hopping conductivity between the CuO planes. The activated behavior of the c axis conductivity supports this interpretation.

Our data clearly shows that the superconductivity and the temperature dependence of the Hall effect are closely related. Note also that the effective carrier concentration (defined as $1/R_He$ here) is about 1 hole per Cu atom in the 2:2:0:1 compound and 0.4 hole per Cu atom in the 2:2:1:2 material. In contrast to the doping studies,[5,6] here the transition temperature does not seem to scale with the carrier density of the CuO layers. One may argue that the Hall coefficient has a temperature dependent enhancement. From a $1/R_He$ vs T plot one can estimate that the "bare value" of 1 hole per Cu atom would be reached at around 1000 K. We want to point out that the comparison of the infrared transmission properties of the 2:2:0:1 and 2:2:1:2 compounds[19] shows an anomaly (characteristic of the superconducting material only) in the midinfrared, around wave numbers of 750 $cm^{-1} \approx 1000$ K. This energy scale seems to be a specific property of the superconducting material.

In conclusion, we demonstrated that the high-temperature superconductor $Bi_2Sr_2CaCu_2O_8$ has a strongly temperature dependent Hall effect, while the structurally similar, metallic (but nonsuperconducting) $Bi_2Sr_2CuO_6$ material has no such behavior. For magnetic fields parallel to the c direction the Hall coefficient is positive, while it can have opposite sign for fields perpendicular to the c direction.

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[1] T. Penney *et al.*, Phys. Rev. B **38**, 2918 (1988).

[2] M. Suzuki *et al.*, Phys. Rev. B **39**, 2312 (1989).

[3] H. Takegi *et al.*, Nature (London) **332**, 236 (1988).

[4] Z. Z. Wang *et al.*, Phys. Rev. B **36**, 7222 (1987).

[5] M. W. Schafer *et al.*, Phys. Rev. B **39**, 2914 (1989).

[6] T. Tamegai *et al.*, Jpn. J. Appl. Phys. **28**, L112 (1989).

[7] R. Reeder *et al.* (unpublished).

[8] C. C. Torrardi *et al.*, Phys. Rev. B **38**, 225 (1988); S. A. Sunshine *et al.*, *ibid.* **38**, 893 (1988); E. A. Hewat, J. J. Capponi, and M. Marezio, Physica C **157**, 502 (1989).

[9] L. Forro and J. R. Cooper, Europhys. Lett. **11**, 55 (1990).

[10] S. N. Artemenko *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **49**, 352 (1989) [JETP Lett. (to be published)].

[11] A. Maeda *et al.*, Phys. Rev. B **41**, 6418 (1990).

[12] S. W. Tozer *et al.*, Phys. Rev. Lett. **59**, 1768 (1987).

[13] L. Forro *et al.*, Solid State Commun. **69**, 1097 (1989).

[14] A. Fert and O. Jaoul, Phys. Rev. Lett. **28**, 303 (1972); A. Fert and A. Hamzic, in *Hall Effect and its Applications*, edited by C. L. Arien and C. R. Westgate (Plenum, New York, 1980).

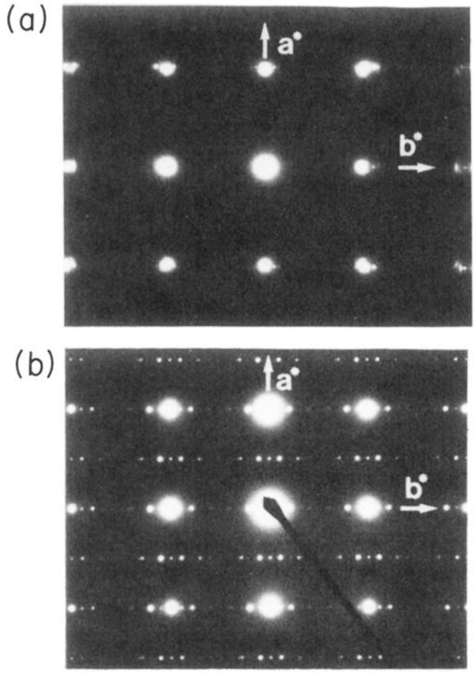
[15] A. T. Fiory and G. S. Grader, Phys. Rev. B **38**, 9198 (1988).

[16] J. Clayhold *et al.*, Phys. Rev. B **39**, 7320 (1989).

[17] N. P. Ong and A. M. Portis, Phys. Rev. B **15**, 1782 (1977).

[18] J. R. Cooper *et al.*, J. Phys. (Paris) **38**, 1097 (1977).

[19] D. Mandrus *et al.* (unpublished).



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