Journal of Magnetism and Magnetic Materials 79 (1989) 146–150
North-Holland, Amsterdam

HALL EFFECT IN HIGH-T_c $Y_1Ba_2Cu_3O_{7-\delta}$ SUPERCONDUCTOR

G.C. VEZZOLI [1]

US Army Materials Technology Laboratory, Emerging Materials Division, Watertown, MA 02172, USA

T. BURKE, B.M. MOON, B. LALEVIC, A. SAFARI, H.G.K. SUNDAR

Rutgers University, Departments of Electrical Engineering and Ceramics, Piscataway, New Jersey, USA

R. BONOMETTI, C. ALEXANDER

US Military Academy, Physics Department, West Point, New York, USA

C. RAU and K. WATERS

Rice University, Department of Physics, Houston, Texas, USA

Received 26 September 1988

We have performed point-by-point and continuous Hall effect experiments as a function of temperature in polycrystalline $Y_1Ba_2Cu_3O_{7-\delta}$. We have shown that the positive Hall constant shows an abrupt increase upon decreasing temperature at a value just above T_c. This temperature corresponds to where the resistance versus temperature data deviates from linearity. At very high fields of 6.8 and 15 T we observe a subsequent decrease in R_H. We interpret these data as supportive of a contribution toward the superconductivity mechanism arising from internal excitons or charge transfer excitations such that the bound exciton concentration increases near T_c at the expense of positive carriers which are reflected in both bound and free holes.

1. Introduction

In this work we address the high-T_c ceramic oxide superconductor [1–5] $Y_1Ba_2Cu_3O_{7-\delta}$ in polycrystalline form shown crystallographically in fig. 1, and believed to be a defect substitutive derivative [6] of the K_2MnF_4 structure [7] (fig. 2) in the form $(Y_1^{3+}Cu_1^{3+})_1(Ba_2^{2+}Cu_2^{2+})_1O_{8-w}$ where for superconductivity $w = 1.1$–1.5.

We studied Hall effect at high B-field in polycrystalline samples in order to study positive hole carriers and relate to hypothesized exciton concentration characteristics. In the absence of large single crystals we were forced to employ ceramic materials. One of the purposes of our work was to determine whether $Y_1Ba_2Cu_3O_{7-\delta}$ would show a peak and trend in positive Hall voltage near T_c as was shown for $LaSrCuO_4$ by Hundley et al. [8]. In

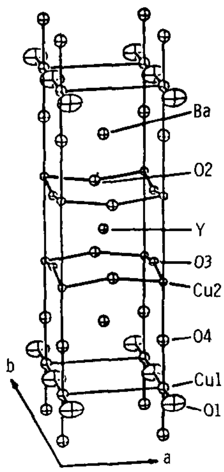

Fig. 1. The crystalline unit cell structure of $Y_1Ba_2Cu_3O_{7-\delta}$.

[1] Visiting Scientist, Materials Science Department, The Massachusetts Institute of Technology, Cambridge, MA 02139, USA.

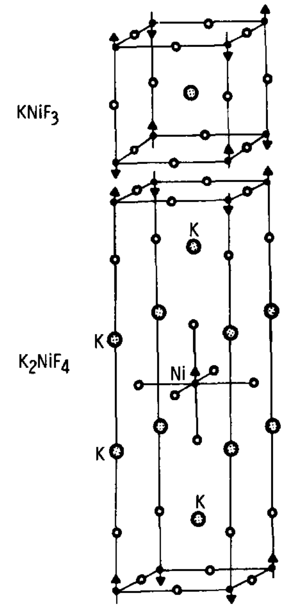

Fig. 2. The crystalline unit cell structure of K_2MnF_4 or Li_2MnF_4.

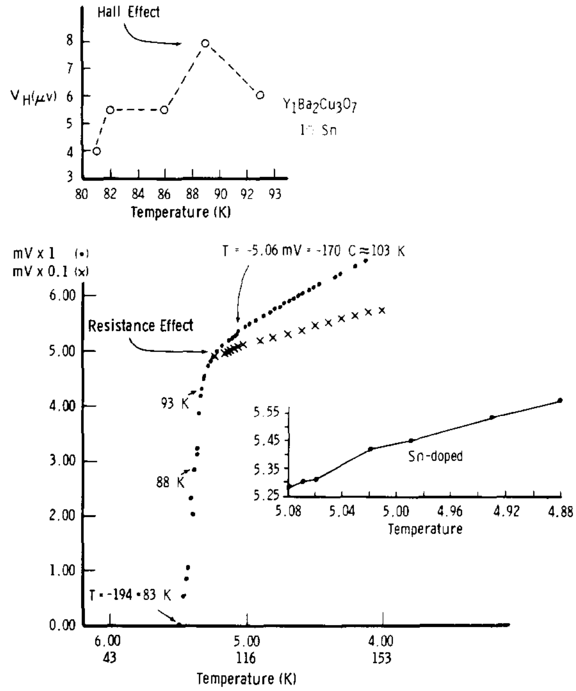

Fig. 3. Hall effect (top) and resistance vs. temperature showing, respectively, increasing $+R_H$ with decreasing temperature approaching T_c, and collapsing resistance starting at T_{onset}.

the latter study the value of R_H became zero then slightly negative at and slightly below T_c.

2. Experimental procedure

Polycrystalline pellets of $Y_1Ba_2Cu_3O_{7-\delta}$ were synthesized at the US Army MTL by Benfer [9] and at Rutgers by Safari et al. [9] employing established methodologies [1–3]. Undoped as well as 1.2% tin- and 1.2% fluorine-added materials were prepared. The experimental configuration employed in this study for the Hall Effect is conventional and all Hall experiments were carried out at the Francis Bitter National Magnet Laboratory at the Massachusetts Institute of Technology. The Hall bar geometry was used.

3. Experimental results and discussion

Hall effect experiments were performed at values of magnetic field to 15 T. Data taken at 6.8 and 5.0 T are given in figs. 3 and 4. These data show a rising positive Hall voltage with decreasing temperature, this effect beginning at temperatures somewhat above T_c (at approximately the temperature (4a) corresponding to the deviation from linear behavior in R vs. T). The results bear *strong* similarity with the peaked signal reported by Hundley et al. [8]. We performed the experiment at 6.8 T in a point by point manner reversing both the current and the magnetic field at each equilibrium temperature. However, so as to preclude missing a maximum or minimum R_H turning-point-temperature we also monitored V_H continuously as a function of temperature for a single polarity of current and magnetic field. This continuous data showed essentially the same trend as the point by point method, proving that stray voltages due to any very-slight mismatch of Hall contacts or thermal emf's were small. Each of our independent measurements (at several temperatures) of V_H at $B = 0$ were less than 1% of our measured Hall signal with $B > 5$ T. In the lower portion of fig. 3 the resistance data on both the undoped and the tin-added samples are given. An

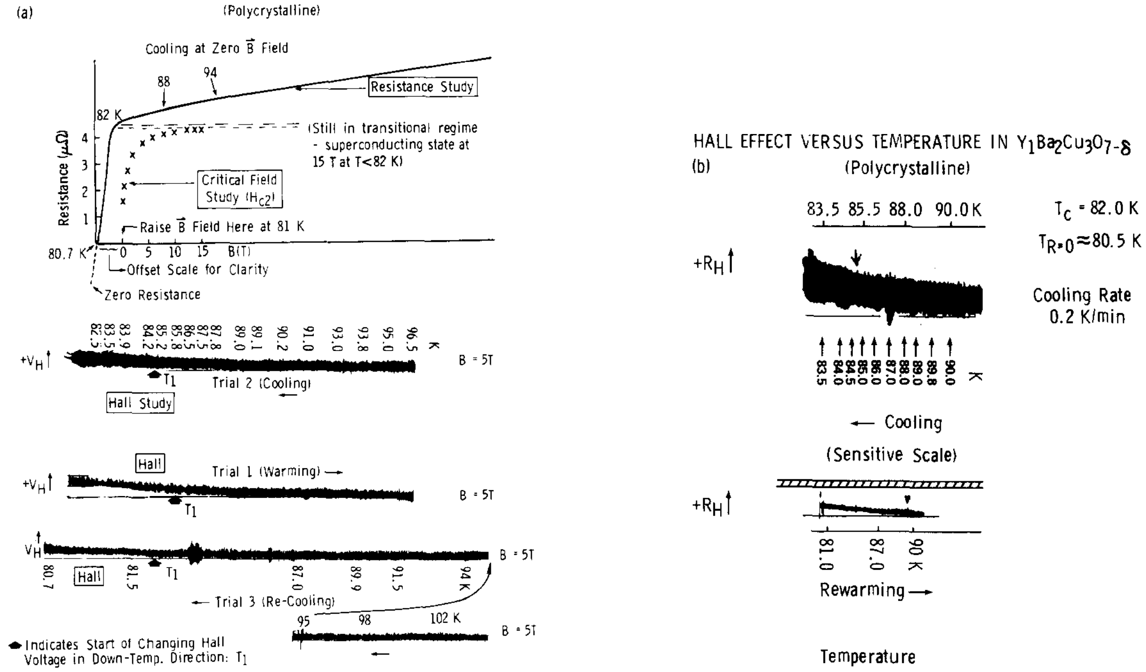

Fig. 4. (a) Resistance vs temperature (cooling) at $B = 0$ and resistance vs. B at $T = 81$ K for $T_c = 82$ K material; lower analogue traces are Hall effect vs. temperature for cooling and heating cycles; (b) Hall voltage vs. cooling at $B = 5$ T showing slope change at arrow.

anomaly is shown in the tin-added sample at about 103 K where a pre-onset effect was observed. EDAX-SEM experiments identified the presence of tin within the grain boundaries. At concentrations greater than about 3 wt% tin there is a clear indication of a second phase. In general, the tin-added material is more machineable than the undoped samples. In fig. 4a we show four-terminal R vs. T data indicating onset in the Rutgers sample at 82.0 K and near-zero resistance

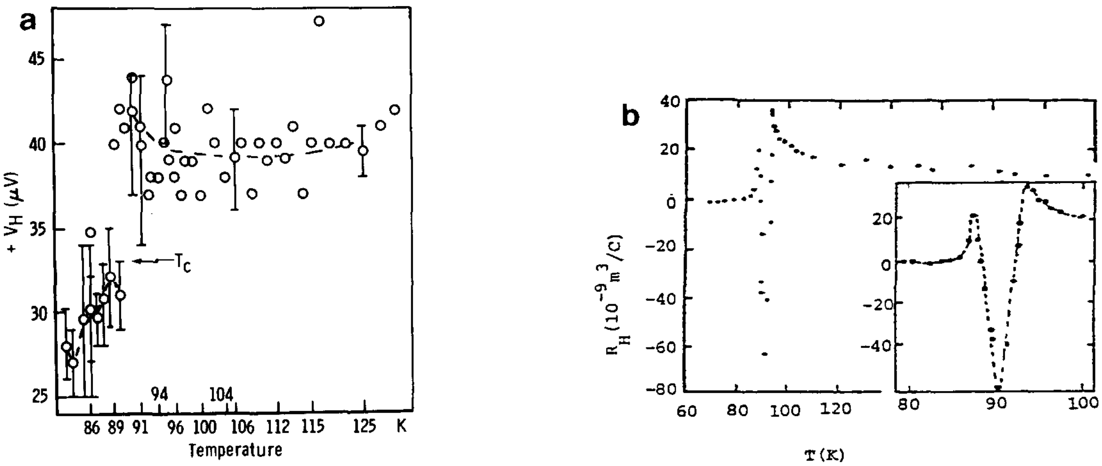

Fig. 5. (a) Hall voltage vs. cooling at 15 T showing abrupt rise near T_c then rapid fall-off; (b) Hall data for $Ba_{1.2}Y_{0.9}V_{0.9}Cu_3O_{7-\delta}$ (from ref. [10]) vs. temperature.

at 80.7 K, using slow cooling rate < 0.30 K/min. In this figure, we also give the recovery of resistance corresponding to the intermediate region between the superconducting and normal states at 81 K as a function of increasing B to 15 T. These data indicate that recovery to the normal state has not occurred even at fields as high as 15 T at temperatures near T_c, and a very strong B dependence of resistance up to 5 T.

In fig. 5a we give our Hall data taken at 15 T which suggest a positive anomaly spike just above T_c, followed by a lowering of $+V_H$ and including some oscillatory or irregular behavior. In fig. 5b we reproduce the data of ref. [10] which shows similar behavior for $Ba_{1.2}Y_{0.9}V_{0.9}Cu_3O_{7-\delta}$ but also includes a region of changes of sign to $R_H < 0$. The data in ref. [10] are explained by the authors as being due to differences between the interior of grains and the grain boundary itself. (The latter can still support a Hall voltage even though the grain "islands" are superconducting.)

If an exciton-mediated mechanism is indeed present as an initiator of high-T_c superconductivity [11], one would expect an *increase* in exciton concentration as the temperature were decreased to the T_c region. This would be expected because of the *increase* in exciton lifetime as heat is withdrawn from the sample. The core of a bound exciton is a positive hole which is either bound on an oxygen, or is due to a charge excitation or fluctuation from one valence state of copper to a second valence state. Thus if exciton concentration increases, there should be a *decrease* in positive local bound carriers which would be reflected by an *increase* in $+R_H$ (as we observe). The decrease in bound holes due to exciton formation could cause a decrease in measured carrier concentration and interfere with the mobility of free holes via a bucket-brigade hopping process [12]. This reasoning, however, might imply a monotonically rising $+V_H$ with decreasing temperature rather than the relatively *sharp* increase that we observe near T_c in figs. 3, 4 and 5. One possible explanation is that Cooper-pairing may cause a decrease in electron-exciton scattering. Such scattering would otherwise be a means to promote recombination of the constituents of the exciton. Further Cooper-pairing may cause an increase in screening between electron and hole, and may further resist recombination. If pairing electron attraction to bound holes exceeds the weak exciton binding energy, then the exciton should ionize. If such a phenomena occurs, it must do so near T_c where Cooper-pairing is rapidly building-up. The result of such an ionization will furnish bound holes and free electrons into the conduction system just prior to reaching the superconducting state. This may account for why there is an observed maximum and a rapid fall-off in the positive Hall signal in the work of Hundley et al. [8], and in the Hall study that we performed at 15 and 6.8 T. Hundley's [8] work and ref. [10] show the Hall signal becoming negative before returning to zero which may imply that so many excitons become ionized that electrons overcome holes in the conduction mechanism. In our work the approximate carrier concentration at the inception of the transition to the superconducting state is $p = 6.0 \times 10^{20}$ holes/cm^3. This is in general agreement with others [10,13,14].

Acknowledgements

We are indebted to Larry Rubin and Bruce Brandt of the National Magnet Laboratory for their cooperative assistance, and to R.N. Katz and R. Harrison of our laboratory for discussions, as well as to Alan Farber of Israel and the microstructure group at ETDL, Ft. Monmouth.

References

[1] C.W. Chu, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang and Y.Q. Wang, Phys. Rev. Lett. 58 (1987) 405.
[2] M.K. Wu, J.E. Ashburn, C.J. Torng, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang, Y.Q. Wang and C.W. Chu, Phys. Rev. Lett. 58 (1987) 908.
[3] P.H. Hor, R.L. Meng, Y.Q. Wang, L. Gao, Z.J. Huang, J. Bechtold, R. Foster and C.W. Chu, Phys. Rev. Lett. 58 (1987) 1891.
[4] J.G. Bednorz and R.A. Mueller, Z. Phys. B64 (1986) 189.
[5] C. Michel, L. Er Rakko and B. Raveau, Mat. Res. Bell. 20 (1985) 667.
[6] G.C. Vezzoli, R. Benfer, W. Spurgeon and J. Bardeen, in: Proc. of Conf. on Novel Mechanisms of Superconductiv-

ity, Berkeley, California, 20-24 June 1987, eds. S. Wolf and V. Kresin (Plenum, New York, 1987).
[7] R.J. Birgeneau, H.J. Guggenheim and G. Shirane, Phys. Rev. B 1 (1979) 2211.
[8] M.F. Hundley, A. Zettl, A. Stacy and M.L. Cohen, Phys. Rev. B 35 (1987) 8800.
[9] R. Benfer, US Army Materials Technology Laboratory, Watertown, MA, A. Safari and H.G.K. Sundar, Rutgers University, Department of Ceramic Science, Piscataway NJ.
[10] Y. Zhao, J. Xia, Zhenhui He, Shitang Sun, Qirui Zhang, Y. Qian, Z. Chen and G. Pan, Chinese Phys. Lett. 5 (1988) 221.
[11] L.V. Keldysh and A.N. Kozlov, JETP Lett. 5 (1967) 190.
V.L. Ginzburg, Contemp. Phys. 9 (1968) 355.
A.P. Russakov, Phys. Stat. Sol. (b) 72 (1975) 503.
A.A. Abrikosov, JETP Lett. 27 (1978) 219.
W.A. Little, J. Low-Temp. Phys. 13 (1975) 365.
D. Allender, J. Bray and J. Bardeen, Phys. Rev. B 8 (1973) 4433.
C.W. Chu, A. Russakov, S. Huang, P.D. Bouger, S. Early, T. Gebale and C. Huang, Phys. Rev. B 18 (1978) 116.
G.C. Vezzoli and J. Bera Phys. Rev. B 23 (1981) 3022.
G.C. Vezzoli, Phys. Rev. B (1982) (in this paper it was suggested that the Cu–O system held more promise than the Cu–Cl system).
[12] J.B. Goodenough, University of Texas, Department of Electrical Engineering, Private Communication.
[13] N.O. Ong, Z.Z. Wang and J. Clayhold, in: Novel Superconductivity, eds. S. Wolf and V. Kresin (Plenum, New York, 1987) p. 1061–1066.
[14] A.I. Braginski, ibid., p. 935–949.
[15] Electron capture experiments tentatively support the view that antiferromagnetic correlations exist in this material.