Anomaly on the temperature dependence of the Hall resistance in semiconducting $YBa_2Cu_3O_{6+x}$ films

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The Hall effect has been studied in semiconducting $YBa_2Cu_3O_{6+x}$ films under equilibrium conditions and also after illumination with visible light. A rounded maximum is observed on the temperature dependence of the Hall resistance, $R_{xy}(T)$. This anomaly shifts down the temperature scale as the density of free carriers increases, because of an increase in the oxygen content x and also because of a photoexcitation of mobile holes (a frozen photoconductivity). It is suggested that the maximum observed on the $R_{xy}(T)$ curves stems from the appearance of an antiferromagnetic order.

The Hall resistance of high-T_c superconductors has an anomalous temperature dependence.[1-3] The temperature dependence of the Hall coefficient in $YBa_2Cu_3O_7$ is approximately $R_H \propto 1/T$.[1,2] Various theoretical models[4-6] have been used to explain the unusually strong temperature dependence $R_H(T)$, observed over such a broad temperature range. However, the problem has yet to be resolved. The temperature dependence of the Hall resistance R_{xy} in $YBa_2Cu_3O_{6+x}$ with an oxygen deficiency, $x<1$, becomes less apparent as the transition to the semiconducting phase, $x \approx 0.4$, is approached.[3] It seemed worthwhile to study the onset and behavior of the anomalous temperature dependence $R_{xy}(T)$ in the semiconducting phase of $YBa_2Cu_3O_{6+x}$ as the oxygen content was raised.

A *frozen photoconductivity* has been observed previously[7,8] near the semiconductor-metal transition ($x \approx 0.4$) in $YBa_2Cu_3O_{6+x}$ films. Prolonged illumination of the films with visible light leads to an increase in their conducting properties; this increase is fully retained when the light is turned off at $T<270$ K. This frozen photoconductivity has been explained on the basis that the light generates additional mobile holes in CuO_2 planes, i.e., on the basis of a *photodoping.*[9] It was shown in Ref. 10 that illumination of $YBa_2Cu_3O_{6+x}$ films at room temperature reduces the Hall component of the resistance, R_{xy}, while it increases the Hall mobility $\mu_H \propto R_{xy}/R_{xx}$. Illumination of $YBa_2Cu_3O_{6+x}$ films has proved to be a very convenient method for introducing progressive, controlled changes in the conducting properties of a sample under given experimental conditions (a given temperature, a given field, etc.). We have accordingly also studied the changes in the temperature dependence of the Hall resistance $R_{xy}(T)$ after illumination of the test samples (i.e., as a result of photodoping).

In these experiments we studied two $YBa_2Cu_3O_{6+x}$ films with two oxygen contents, 1) $x=0.33$ and 2) $x=0.36$, on $SrTiO_3$ substrates. The desired oxygen content x in the $YBa_2Cu_3O_7$ superconducting films was achieved by annealing the films for several hours at 360°C at an oxygen pressure corresponding to the $P_{O_2}(x, T)$ equilib-

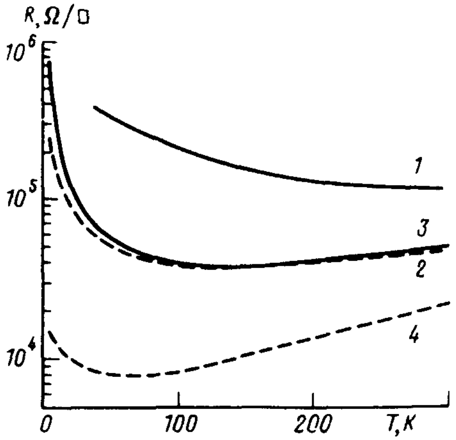

FIG. 1. Temperature dependence of the resistance, $R_{xx}(T)$, of $YBa_2Cu_3O_{6+x}$ films for $x=0.33$ (curves *1* and *2*) and $x=0.36$ (curves *3* and *4*) before (solid curves) and after (dashed curves) prolonged illumination. The resistances are expressed per conducting CuO_2 plane.

rium diagram.[10] The c axis of the films was oriented perpendicular to the surface of the substrate. The thickness of the films was 80 nm. The oxygen concentration in the $YBa_2Cu_3O_{6+x}$ films was found from x-ray measurements, specifically, from the lattice constant c, within absolute and relative errors $\Delta x=0.05$ and 0.01, respectively. A magnetic field up to 7 T was produced by a superconducting solenoid. The samples has special silver contacts for independent measurements of the longitudinal and Hall resistances. The measurements were carried out at a direct current. The Hall voltage was measured by two methods: 1) The first was the Van der Pauw method, with a cyclic interchange of the potential and current contacts[11] in a given magnetic field $H=5$ T. In this case we use the formula $R_{xy}=(1/2)\cdot(U_{24}/I_{13}-U_{13}/I_{24})$ (here 13 and 24 specify the current and potential contacts). 2) The second was the conventional method involving a variation in the direction of the magnetic field. In this case we use the formula $R_{xy}=(1/2)\cdot[R(H)-R(-H)]$. The first method yields continuous measurements of the temperature dependence $R_{xy}(T)$ or of the time evolution $R_{xy}(t)$ during the illumination. This method is thus more accurate. However, the Van der Pauw method is valid only for a linear system; it generates incorrect results if the properties of the electric contacts deviate from linearity. Accordingly, the Hall voltage in film 1, with the lower oxygen content, was measured by the second method at $T<200$ K. In other cases, no problems arose from the contacts, and we used the first method. The validity of the results measured by the Van der Pauw method were monitored both in a zero field, on the basis of the condition $R_{xy}(0)=0$, and in some sampling measurements by classical method 2. The field dependence of the Hall effect was linear for both films over the entire temperature range studied, 4.2–300 K. The films were illuminated with a He–Ne laser ($\lambda=632.8$ nm) with a flux density of 0.1 W/cm^2.

Figure 1 shows the equilibrium (pre-illumination) temperature dependence of the longitudinal resistance, $R_{xx}(T)$, for both films (solid curves). The resistance R_{xx} of film 1 increases monotonically with decreasing temperature over the entire measurement range, 4.2–300 K. The resistance of film 2 initially falls off slightly with the

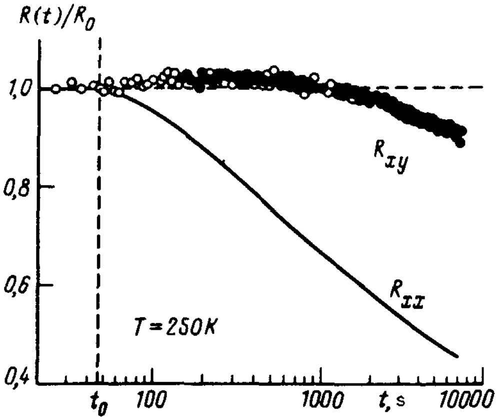

FIG. 2. The longitudinal component $R_{xx}(t)$ (solid curve) and the Hall component R_{xy} (points) of the resistance of a $YBa_2Cu_3O_{6.33}$ film versus the illumination time at $T=250$ K and $H=5$ T ($\lambda=632.8$ nm, light flux density of 0.1 W/cm^2). Here t_0 is the time at which the illumination begins.

temperature, but below 140 K the localization of free carriers (holes) leads to a strong semiconducting increase in R_{xx}. Illumination of the films leads to a metastable increase in their metallic properties.[9] After prolonged illumination, the resistance of the films falls off by a factor of 2 or 3, and the semiconducting increase in the resistance at low temperatures is substantially suppressed (the dashed lines in Fig. 1).

Figure 2 shows some typical curves of both components of the resistance versus the time, $R_{xx}(t)$ and $R_{xy}(t)$, for film 1 at an illumination temperature of 250 K. We see that the temperature dependence of the Hall resistance, $R_{xy}(t)$, differs significantly from the temperature dependence $R_{xx}(t)$, even at a qualitative level.[10] The longitudinal resistance R_{xx} begins a sharp decrease immediately after the light is applied, at any given temperature. In all cases, the rate of decrease of the resistance, dR_{xx}/dt (the effectiveness of the illumination), decreases monotonically with illumination time.[9] The Hall component of the resistance, R_{xy}, in contrast, changes only negligibly or even increases slightly in the initial stage of the illumination. Only after a prolonged illumination does it begin to decrease monotonically. The rate of change of the Hall resistance, dR_{xy}/dt, may even increase after a long illumination time. A similar behavior was found for film 2, but there was the distinction that the increase in the Hall resistance during the illumination was observed only at illumination temperatures of 140–240 K.

Figure 3 shows the temperature dependence of the Hall resistance, $R_{xy}(T)$, measured before and after prolonged illumination. The experimental curves are clearly anomalous. Before the illumination, the Hall resistance of film 1 goes through a rounded maximum at $T_{\max}\approx 265$ K and then decreases as the temperature is lowered, by a factor of 2 at $T=80$ K. After a prolonged illumination of film 1 ($x=0.33$), the $R_{xy}(T)$ curve becomes smoother, with a rounded maximum at $T_{\max}\approx 220$ K. Interestingly, the substantial increase in the conductivity in film 1 (Fig. 1) due to the photogeneration of additional mobile holes at $T<150$ K leads to an increase in the Hall resistance R_{xy} instead of a decrease (Fig. 3a).

Figure 3b shows the results of measurements of the temperature dependence of the Hall resistance, $R_{xy}(T)$, of film 2, with the higher oxygen content, $x=0.36$. Before

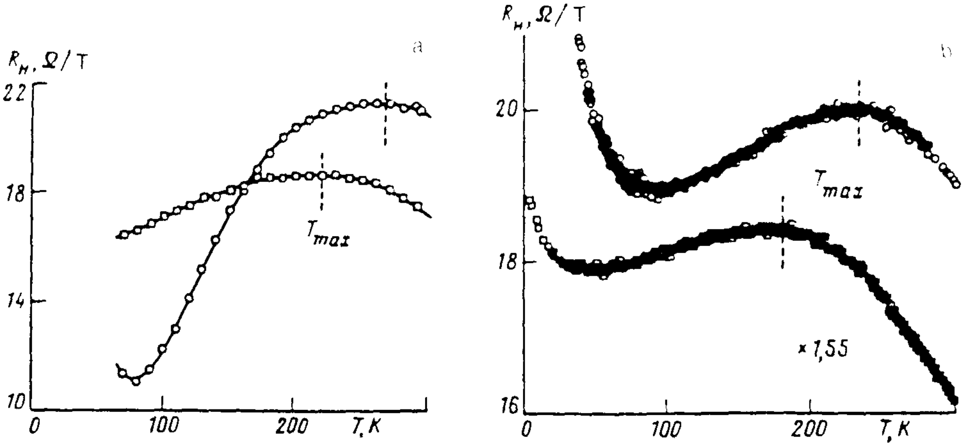

FIG. 3. Temperature dependence of the Hall resistance, $R_{xy}(T)$, before (o) and after (□) prolonged illumination in a magnetic field $H=5$ T. a—Film 1, $x=0.33$; b—film 2, $x=0.36$ (the data obtained on R_{xy} for film 2 after the illumination have been multiplied by a normalization coefficient of 1.55). The resistances are expressed per conducting CuO_2 plane.

the illumination, we again observe a rounded maximum on the $R_{xy}(T)$ curve, at $T_{\max}\approx 230$ K. At $T<100$ K the Hall resistance of film 2 begins to increase rapidly, because of a localization of free carriers at low temperatures [cf. $R_{xx}(T)$ in Fig. 1]. After prolonged illumination of film 2, the average value of the Hall resistance decreases by a factor of about 1.5. A more detailed analysis of the experimental data shows that the maximum on the $R_{xy}(T)$ curve of film 2 after illumination shifts to a lower temperature, $T_{\max}\approx 180$ K (Fig. 3b). The low-temperature localization of holes after illumination is suppressed. The temperature dependence of the longitudinal resistance $R_{xx}(T)$ exhibits no structural feature near $T_{\max}$ for either film.

We can thus draw the following conclusion from this study. The Hall effect in the $YBa_2Cu_3O_{6+x}$ films is characterized by an anomalous temperature dependence in not only the metallic phase[1-3] but also the semiconducting phase. The curves of $R_{xy}(T)$ have a rounded maximum, which shifts to lower temperatures with increasing density of free carriers in the sample, because of an increase in the oxygen content x and also because of a photogeneration of additional free holes in the course of the illumination.

The compound $YBa_2Cu_3O_6$ is known[12] to be an antiferromagnet with $T_N=415$ K. An increase in the hole density in the CuO_2 planes leads to a rapid suppression of the long-range magnetic order and to a decrease in T_N, to the point that it vanishes at $x=0.4$. We would suggest that the maxima observed on the temperature dependence of the Hall resistance in these films are due to the onset of an antiferromagnetic order. According to the $YBa_2Cu_3O_{6+x}$ phase diagram, the Néel temperature[12] at oxygen concentrations $x=0.33$ and 0.36 are $T_N=295$ and 240 K, respectively. At these temperatures we see the rounded maximum on the $R_{xy}(T)$ curves (Fig. 3); i.e., we have $T_{\max}\simeq T_N$ at our accuracy level. The shift of the maxima on the $R_{xy}(T)$ curves after the illumination of the samples also agrees with the idea of a disruption of a long-range order (and of a lowering of T_N) by free carriers excited by the light.

The presence of maxima near T_N on the $R_{xy}(T)$ curves explains the "strange" nonmonotonic behavior of the Hall resistance component R_{xy} during illumination at $T < T_N$ (Fig. 2). With an increase in density of photoexcited mobile holes in the films, two distinct factors affect the value of R_{xy}. On the one hand, the increase in the number of carriers, n, should lower the average value in accordance with $R_{xy} \propto n^{-1}$. On the other hand, this increase in the number of carriers leads to a decrease in T_N and thus a shift of the maximum on the $R_{xy}(T)$ curve to a higher temperature. As a result, for small doses of light the second factor is predominant, and R_{xy} increases slightly despite the increase in the number of mobile holes, n. At $T > T_N$, R_{xy} always decreases in magnitude during illumination.[10]

In general, the following factors could be cited as possible reasons for the appearance of a maximum on the Hall resistance near the temperature of the antiferromagnetic transition: 1) a "magnetic" localization of free carriers near $T = T_N$; 2) a scattering of holes by magnetic fluctuations and impurities.

The first of these possibilities looks unlikely, because (first) the decrease in the density free carriers would have to reach 50% (Fig. 3), and (second) it would be difficult to expect a pronounced further localization of charges at such high temperatures, $T > 150$–200 K.

The second possibility looks more realistic. We know that the spin-orbit coupling leads to an asymmetric (in the left-right sense) scattering of electrons by impurities with a time τ_{sk} and thus a contribution to the Hall effect (the "skew scattering mechanism"[1,4,13]): $R_{xy} \propto n^{-1}\tau_{sk}^{-1}(T)$. The temperature dependence of the Hall effect in heavy-fermion systems has been explained previously[13] on the basis of this mechanism. It was suggested in Ref. 4 that the anomalous temperature dependence $R_{xy}(T)$ of $YBa_2Cu_3O_7$ might also be caused by an asymmetric magnetic scattering. In the case of uncorrelated magnetic impurities, the additional contribution to R_{xy} from the asymmetric scattering would be proportional to the susceptibility of the magnetic moments of the impurities: $R_{xy} \propto \chi R_{xx}$. In $YBa_2Cu_3O_{6+x}$, the magnetic impurity moments undoubtedly undergo a strong interaction with each other through the antiferromagnetic CuO_2 subsystem. In practice, therefore, this simple relationship would not prevail.[1] Nevertheless, one can make the qualitative assertion that the rate of asymmetric scattering by magnetic impurities, τ_{sk}^{-1}, should increase near T_N, and that this increase may lead to the appearance of a maximum on the $R_{xy}(T)$ curves in the semiconducting phase of $YBa_2Cu_3O_{6+x}$. The contribution of *asymmetric* scattering to the longitudinal resistance R_{xx} is not predominant (in comparison with the ordinary *symmetric* scattering by magnetic fluctuations, phonons, and impurities), and it would not cause any significant anomaly on the $R_{xx}(T)$ curves.

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