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Hall Effect of Silver Ions in $RbAg_4I_5$ Single Crystals

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The Hall effect of the high ionic conductor $RbAg_4I_5$ was studied from 0 to 40°C. By comparison with the results on photoexcited carriers, it is determined that the origins of Hall signals in $RbAg_4I_5$ are the mobile silver ions. The value of Hall mobility is about 0.05 $cm^2\ V^{-1}\ sec^{-1}$ at room temperature, which is about 30 times as large as that of the ions in NaCl at 780°C previously obtained by Read and Katz.

There have been many Hall-effect studies concerning the electrons and the holes in ionic crystals and semiconductors by using various techniques.[1] However, no previous study has been conducted on the Hall effect of ions in a solid except for one in NaCl single crystals at a high temperature by Read and Katz[2]; the sodium ions were supposed to be the primary origin of the voltage. Hall-effect measurements of ions in a solid are very difficult, because it is suspected that the ionic carriers spend an appreciable time in a stable status in the lattice and that they possess very heavy masses and very large volumes compared with those of electronic carriers. Furthermore, the space charge near the electrodes arising from the movement of ions under an electric field causes additional difficulties in taking measurements.

Recently, several scientists[3] investigated high-ionic-conducting solid electrolyte rubidium silver iodide $RbAg_4I_5$, which has an ionic conductivity of about 0.2 $\Omega^{-1}\ cm^{-1}$ at room temperature. Using the Tubandt method, it was determined that the charge-carrying species in $RbAg_4I_5$ were the silver ions and their transport number was about 0.995.[4] This high ionic conductivity was assigned mainly due to the isostructural lattice of $RbAg_4I_5$. The purpose of this work is to study the behavior of silver ions in $RbAg_4I_5$ single crystals by Hall-effect measurements.

The Hall effect in $RbAg_4I_5$ was investigated by a new technique[5] which was essentially an ac method to prevent the accumulation of space charges near electrodes; the alternating current $I(f_1)$ through a sample and the alternating applied magnetic field $H(f_2)$ were phase locked to each other. Thus, the observed Hall voltage oscillated with a frequency of the sum or the difference of f_1 and f_2. Actually, f_1 and f_2 were 75 and 50 Hz, respectively. A component with 125 Hz in the Hall voltage was selected and amplified by a low-noise preamplifier with a pass filter followed by a lock-in amplifier. Square-shaped samples with four electrodes were investigated over a temperature range from 0 to 40°C. It was confirmed that the measuring system used in this experiment was able to detect a Hall voltage as low as around 1 nV, about 50 times as sensitive as the method used by Read and Katz.[2] The validity of this technique was confirmed by performing the same measurements on *n*-type Ge specimens whose electronic properties were studied by independent experiments.

Single crystals of $RbAg_4I_5$ as large as 1 cm diam × 4 cm long were grown from melts by the Czochralski technique.[6] Extrapure reagents AgI and RbI were purified by vacuum distillation and then by zone melting. The crystals obtained were transparent with a light yellow tint. Sizes of the specimens were about $6\times6\times0.5$ mm^3.

Hall voltages in $RbAg_4I_5$ single crystals in the dark are linear with respect to the applied fields —both magnetic and electric. Hall mobility μ_c in the dark is shown in Fig. 1 as a function of the reciprocal temperature. The value of μ_c increases with increasing temperature, and is about 0.05 $cm^2\ V^{-1}\ sec^{-1}$ at room temperature which is approximately 30 times as large as that of the ions in NaCl single crystals at 780°C obtained by Read and Katz.[2]

Measurements of the Hall effect and conductivity under photoexcitation were effected to confirm that origins of the Hall data presented in Fig. 1 were the silver ions in $RbAg_4I_5$. Since the wave-

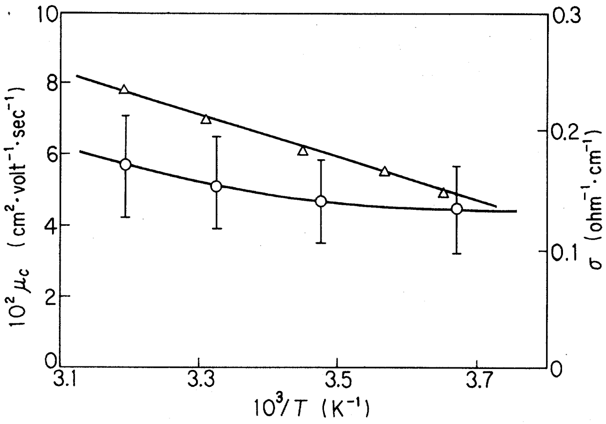

FIG. 1. Hall mobility μ_c (circles) and conductivity σ (triangles) of silver ions in $RbAg_4I_5$ in the dark as a function of reciprocal temperature.

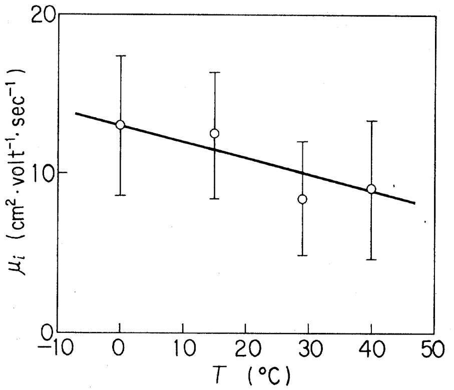

FIG. 2. Hall mobility μ_i of photoexcited carriers in $RbAg_4I_5$ as a function of temperature.

length of the fundamental optical absorption edge in $RbAg_4I_5$ was about 400 nm at room temperature, light from a high-pressure mercury lamp was used to produce the photoexcited carriers in addition to the silver ions which existed when it was in the dark. The ordinary two-carrier analysis of Hall signals in the steady state[7] was applied to evaluate Hall mobilities for cations and electronic carriers. The sign of Hall voltage under illumination was found to be opposite to that in the dark, and the absolute values were comparable with each other. The conductivity at 0°C changed by some 0.5% under photoexcitation. The weight-averaged Hall mobility μ_i of the photoelectrons and holes derived from the above analysis is shown in Fig. 2 as function of the temperature. As the temperature increases, the magnitude of μ_i decreases in the same manner as that of Hall mobility in other ionic crystals under photoexcitation.[8] The value of μ_i at room temperature is about 9 $cm^2\ V^{-1}\ sec^{-1}$ in the present case. By virtue of the sign of Hall voltage and the magnitude and temperature dependence of Hall mobility, it is concluded that the photoelectrons primarily contribute to Hall signals under illumination. On the other hand, the Hall mobility of the holes in ionic crystals is about 0.03 times as large as that of the electrons at room temperature, and is nearly proportional to the minus fourth power of the temperature in this region[9] with increased dependence on temperature over that of the electrons. The above observations, such as the sign of Hall voltage, and the magnitude and the temperature dependence of Hall mobility, suggest that Hall signals in the dark are caused by ionic carriers instead of electronic carriers. On the other hand, it has been known that silver ions are the only movable ionic carriers in this temperature range.[10] Therefore, it may be naturally concluded that the origins of Hall signals in $RbAg_4I_5$ single crystals in the dark are the silver ions.

Hall mobility of silver ions in $RbAg_4I_5$ may be explained in terms of a small-polaron model made by Emin and Holstein[11]; the motions of both are thought to be predominantly effected by random jumping between neighboring sites of the lattice. In the classical limit, the Hall mobility μ_c of the silver ions can be represented by the formula

$$\mu_c = \frac{ea^2}{4\pi} \frac{J}{\hbar KT} F(T) e^{-(\epsilon - 3J)/3KT}, \tag{1}$$

where a is the lattice constant, J is the overlap energy between the nearest-neighbor sites, T is the temperature, ϵ is the activation energy corresponding to an energetic coincidence of two sites, $F(T)$ is a dimensionless function of temperature, and K is the Boltzmann constant. Since the sixteen silver ions in a unit cell of $RbAg_4I_5$ are thought to be distributed over three crystallographically nonequivalent sets of 56 sites,[12] and the magnitude of both site-energy differences and mutual repulsion of the silver ions on the nearest-neighbor sites is comparable with that of thermal energies at room temperature,[13,14] there are uniformly possible positions of the silver ions in a certain plane. Therefore, the approximate calculation of μ_c can be carried out on the close-packed lattice of the silver ions or the triangle lattice. The following values are assumed: a is chosen as $[11.4/(56)^{1/3}] \times 10^{-8}$ cm,[12] ϵ is given as 0.09 eV, whose value is obtained from the dark conductivity as shown in Fig. 1. J is chosen as $K\Theta$, where Θ is the Debye temperature 92 K.[15] $F(T)$ is set equal to unity.[11] Then, we have $\mu_c \simeq 0.04\ \mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{sec}^{-1}$ at room temperature, which is considered to be reasonable as compared with the observed.

However, according to Emin-Holstein theory, the conductivity σ is written as

$$\sigma \simeq 3\, ne\mu_c e^{-2\epsilon/3KT}, \tag{2}$$

where n is the effective carrier density equal to the actual density of silver ions. Inserting the experimental values of μ_c and ϵ, the experimental conductivity as shown in Fig. 1 is at least an order of magnitude less than the theoretical estimate. It would appear that only a fraction $\lesssim 10\%$ of the silver ions are effective carriers. This result is in contradiction with the conclusions of Refs. 13 and 15, which claim that the silver ions are randomly distributed among all of the available sites. Although the reason for such contradictions is not elucidated, it is noticed that the value and temperature dependence derived from Eq. (1) agree with those observed within the experimental errors.

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Dielectric Constant of an Exchange-Polarized Electron Gas and the Metal-Semiconductor Transition in Doped EuO

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This paper reports calculations of the linear responses (the dielectric constant and the magnetic susceptibility) of an electron gas interacting through an exchange interaction with a set of localized magnetic moments. This allows one to account for the metal-semiconductor transition which has been observed in moderately doped EuO, in agreement with experimental data.

Some of the peculiar properties of magnetic semiconductors may be understood within the framework of a simple model: An electron gas is embedded in a lattice of localized magnetic moments; magnetic order is ensured by direct interaction between magnetic moments, but the conduction electrons are able to interact with the magnetic moments through an exchange interaction. This interaction is expected to modify both the electronic and the magnetic properties of the system.[1] It is of interest to draw all the inferences from this model and particularly to study the response of the system to some external perturbation. We thus present a simple derivation of the k-dependent dielectric constant and susceptibility.

Actual magnetic semiconductors are rather extrinsic than intrinsic ones, i.e., the conduction