the experiments.

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[1] J. C. Fisher and I. Giaever, J. Appl. Phys. (to be published).

[2] I. Giaever, Phys. Rev. Letters 5, 147 (1960).

[3] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

[4] I. Giaever, Proceedings of the Seventh International Conference on Low-Temperature Physics (to be published).

IONIC HALL EFFECT IN SODIUM CHLORIDE*

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(Received October 11, 1960)

High-temperature ionic Hall effect measurements in large single crystals of pure sodium chloride were undertaken in order (a) to demonstrate the existence of the Hall effect due to the motion of ionic charge carriers, and (b) to provide an independent measurement of the temperature dependence of the mobility of the ionic charge carriers in sodium chloride.

The ionic Hall effect has previously never been observed in a solid, although an upper limit for the effect in NaCl has been set.[1]

Two ionic drift-mobility measurements in NaCl exist, but neither measurement was carried out near the melting point.[2,3] Both measurements used the impurity-doping method of Koch and Wagner[4] and are subject to the uncertainties implicit in this method.[5] The two experiments, which measured the drift mobility of the sodium ions, gave results which are in only rough agreement with each other.

Hall effect measurements provide a more straightforward means of measuring the mobilities of the ionic charge carriers in NaCl and other ionic conductors and are limited only by the smallness of the effect.

The ionic Hall effect arises from the action of the magnetic field on the asymmetry in the motion of the ionic charge carriers set up by the applied electric field. It can be shown[6] that a nonzero net transverse jump probability exists, and that the temperature dependence of the Hall mobility has the same form as that of the drift mobility. The relationship between the measured rms Hall voltage V_H and the Hall mobility μ_H, in the case where ac applied fields and a square sample are used, is

$$\mu_H = 2.10\, V_H/VB \text{ (meter}^2\text{/volt-sec)},$$

where the correction for the end effect[7] has been included. Here, V is the rms voltage of the applied electric field and B is the rms flux density of the magnetic field.

We used the ac cross-modulation method[8] to make Hall measurements in Harshaw NaCl. The electric and magnetic fields were applied at 85 and 60 cps, respectively, and the 25-cps Hall voltage difference frequency was measured. Square samples and the usual four-electrode configuration were used. The Hall voltage measurement system was able to measure signals as low as 0.05 μv. The linearity of this system was assured by the use of ultralinear cathode follower[9] input stages. Elaborate precautions were taken to insure that no spurious 25-cps signals were produced in the equipment. Also, the environment of the sample was maintained so that no electronic conduction was induced in the sample.

In spite of the presence of a large amount of current noise in the crystal, Hall measurements were made at seven temperatures in the range 610-780°C. The observed Hall voltage was proportional to the magnitude of the applied fields and was not sensitive to the pressure applied on the electric field or Hall electrodes. The apparent Hall mobility (which is the difference between the Hall mobilities of the sodium and chlorine ions) calculated from these measurements is shown in Fig. 1.

The experimental points are fitted by the curve shown in Fig. 1. The shape of this curve is derived from the diffusion data of Laurent and Benard.[10]

In Fig. 2 we have compared our apparent Hall mobility data with extrapolations of the sodium ion drift mobility measurements of Etzel and Maurer[2] and of Bean.[3] The results of Etzel and Maurer as corrected by Lidiard[11] are also given in Fig. 2. The proportionality of the observed Hall voltage to the applied fields is exhibited by the low-field Hall data plotted in Fig. 2.

The Hall data are not accurate enough to permit resolution of the mobilities of the sodium and chlorine ions. However, by extrapolating from the low-temperature portion of the curve, it is

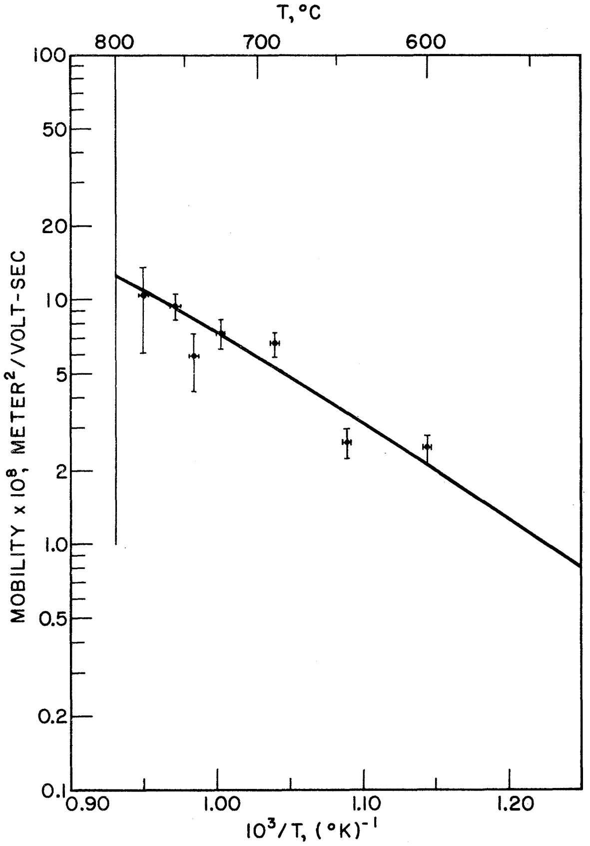

FIG. 1. Hall mobility measurements in NaCl.

possible to make a rough estimate of the Hall mobility of the sodium ions in NaCl. The activation energy E and the pre-exponential coefficient A, defined by the equation $\mu_H = AT^{-1} \exp(-E/kT)$, are found in this way, and are given in Table I. The same type of temperature dependence is customarily applied to the analysis of drift mobility data. For comparison, the values found by the drift mobility measurements and the result of the calculation of the activation energy by Guccione et al.[12] are also given.

Table I. Values of the activation energy and the pre-exponential coefficient in the mobility expression for sodium ions in NaCl.

Source	Activation energy ev	Pre-exponential coefficient (meter)^2-°K/volt-sec
Present work	0.87 ±0.10	$2.0^{+8}_{-1.5}$
Etzel and Maurer	0.85	1.96
Etzel and Maurer (Lidiard)	0.84	2.12
Bean	0.78	0.46
Guccione et al.	0.87	...

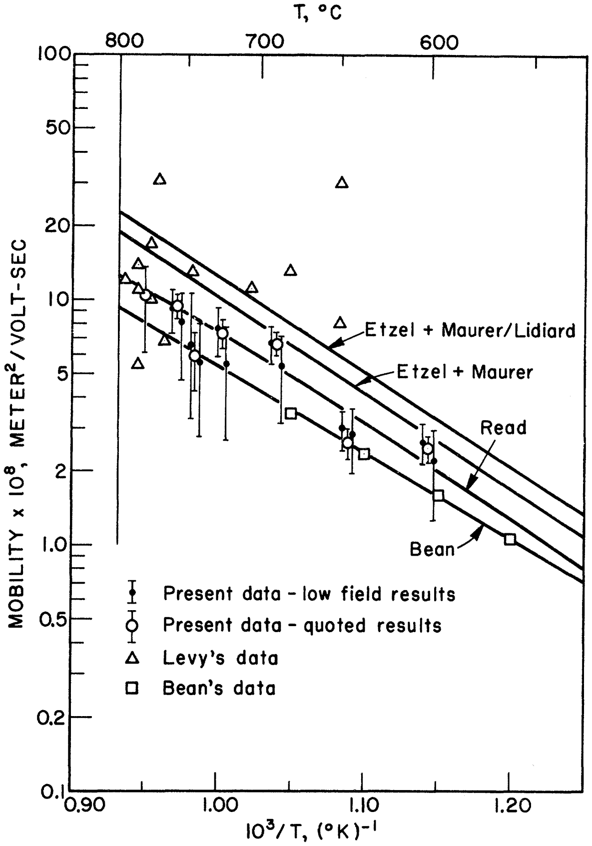

FIG. 2. Comparison of Hall data with previous mobility measurements in NaCl. The "quoted" results are identical with those of Fig. 1. They were obtained with the highest electric and magnetic fields, and are more accurate than the low-field results. The latter are included for completeness and as a check for the proper field dependences of the measured Hall voltage.

These measurements, according to our interpretation of the observed signals, represent the first observations of the ionic Hall effect in a solid. They are within the upper limits set by Levy[1] (see Fig. 2). The Hall mobility results are in the same range as the extant drift-mobility data and provide a rough verification of these previous results. In addition, the approximate equality of the Hall and drift mobilities of the ionic charge carriers in NaCl is demonstrated.

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*This research was supported by a contract of the U. S. Navy Department through the Office of Naval Research. It is based on a thesis submitted by Philip

L. Read in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics at the University of Michigan, 1960.

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[1] J. L. Levy, Phys. Rev. 92, 215 (1953).

[2] H. W. Etzel and R. J. Maurer, J. Chem. Phys. 18, 1003 (1950).

[3] C. P. Bean, thesis, University of Illinois, 1952 (unpublished).

[4] E. Koch and C. Wagner, Z. physik. Chem. B38, 295 (1937).

[5] A. B. Lidiard, Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, p. 246 ff.

[6] P. L. Read and E. Katz (to be published).

[7] I. Isenberg, B. R. Russel, and R. F. Greene, Rev. Sci. Instr. 19, 685 (1948).

[8] B. R. Russel and C. Wahlig, Rev. Sci. Instr. 21, 1028 (1950).

[9] P. L. Read, Rev. Sci. Instr. (to be published).

[10] J. Laurent and J. Benard, J. Phys. Chem. Solids 3, 7 (1957).

[11] A. B. Lidiard, Phys. Rev. 94, 29 (1954).

[12] R. Guccione, M. P. Tosi, and M. Asdente, J. Phys. Chem. Solids 10, 162 (1959).

SPIN HAMILTONIAN OF Co^{2+}

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(Received October 4, 1960)

The conventional spin Hamiltonian for an ion with $S=3/2$ at a crystalline site of cubic or tetrahedral symmetry is

$$\mathcal{H}_0 = g\beta\vec{S}\cdot\vec{H} + A\vec{S}\cdot\vec{I} - g_N\beta_N\vec{I}\cdot\vec{H}, \tag{1}$$

if the lowest orbital state of the ion is a singlet. This approximate result, derived by Abragam and Pryce,[1] has generally sufficed to describe the results of experiment. Symmetry, however, permits additional terms and, as Koster and Statz[2] and Bleaney[3] have pointed out, there should be situations[4] for which it is necessary to augment $\mathcal{H}_0$ with the terms

$$u\beta\{S_x{}^3H_x + S_y{}^3H_y + S_z{}^3H_z - \tfrac{1}{5}(\vec{S}\cdot\vec{H})[3S(S+1)-1]\}$$
$$+U\{S_x{}^3I_x + S_y{}^3I_y + S_z{}^3I_z - \tfrac{1}{5}(\vec{S}\cdot\vec{I})[3S(S+1)-1]\}, \tag{2}$$

where x, y, and z are the cubic axes of the crystal. In this Letter we report experimental results demonstrating the importance of these new terms for the spectrum of Co^{2+} in certain crystals. We also give an elementary derivation showing that one can predict the correct order of magnitude of the new terms from interactions with excited states.

If $g\beta\vec{S}\cdot\vec{H}$ is large compared with all other terms in the spin Hamiltonian and if $A\vec{S}\cdot\vec{I}$ is larger than the other terms involving $\vec{I}$, the energy levels to first order in A, u, and U are

$$W_{Mm} = g\beta HM + AMm - g_N\beta_N Hm$$
$$+(u\beta H + Um)\{M^3 - \tfrac{1}{5}[3S(S+1)-1]M\}p, \tag{3}$$

where M and m are the eigenvalues of the components along $\vec{H}$ of $\vec{S}$ and $\vec{I}$, respectively, and where

$$p = 1 - 5(n_1{}^2n_2{}^2 + n_2{}^2n_3{}^2 + n_3{}^2n_1{}^2). \tag{4}$$

Here n_1, n_2, and n_3 denote the direction cosines of $\vec{H}$ with respect to the cubic axes. The spin resonance transitions for $S=3/2$ are:

$M=+1/2$ to $-1/2$:

$$h\nu = [g-(9/5)up]\beta H + [A-(9/5)Up]m, \tag{5a}$$

$M=\pm3/2$ to $\pm1/2$:

$$h\nu = [g+(6/5)up]\beta H + [A+(6/5)Up]m. \tag{5b}$$

Cobalt was introduced into natural single crystals of CaF_2 and (cubic) ZnS and into synthetic single crystals of CaF_2, CdTe, and ZnSe by diffusion from suitable powders. Synthetic single crystals of ZnTe and ZnS doped with cobalt were also studied. The coordination about the metal ions is eightfold and cubic in CaF_2; in the other crystals it is fourfold and tetrahedral. The spin resonance spectrum of Co^{2+} consisted in each case of one fine-structure transition, which is assumed to be the $M=+1/2$ to $-1/2$ transition. This transition is unaffected by small noncubic terms in the Hamiltonian associated with crystalline strains. Such terms are presumed to broaden the $M=\pm1/2$ to $\pm3/2$ transitions beyond detection.

In accordance with (5a) the spectra are observed to be anisotropic: They can be described