# Galvanomagnetic Properties of $n$-Type $CdAs_2$

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Galvanomagnetic measurements on oriented, single crystals of $n$-type $CdAs_2$, a noncubic semiconductor, indicate the surfaces of constant energy to be ellipsoids of revolution, located along the symmetry axis of the crystal system. The ratio of electronic mobility is found to be $\mu_{II}/\mu_{\perp}\sim 4$, from Hall and resistivity data. Magnetoresistance measurements confirm this conduction-band model and indicate the scattering to be due primarily to acoustical lattice modes with some degree of impurity scattering.

## INTRODUCTION

WHILE attempts at preparation of the various noncubic II–V semiconductors have been extensive,[1,2] detailed electrical measurements, on oriented single crystals of semiconductor purity, have been limited.[3–6] This is particularly true in the case of $n$-type $CdAs_2$. The present work outlines the results of some recent electrical measurements.

Parts I and II of this paper discuss, respectively, the experimental procedure and the data obtained. Measurements made to ascertain the degree of anisotropy of the Hall coefficient are outlined in Part I. In Part II it is shown that within the accuracy of the experiment the Hall coefficient is independent of crystal orientation and the longitudinal magnetoresistance is negligible. It is shown in Part III that these results are consistent with a simple conduction-band model. The resistivity can then be used to obtain the ratio $K=\tau_{II}m_{\perp}/\tau_{\perp}m_{II}$ where $m_{\perp}$ and $m_{II}$ are the electronic effective masses perpendicular and parallel to the fourfold symmetry axis and $\tau_{\perp}$ and $\tau_{II}$ the relaxation times.

## I. EXPERIMENTAL

Measurements were made on oriented single-crystal parallelepipeds. Sample alignment was maintained relative to the magnetic field so as to allow the sample to be rotated about a single axis of the laboratory coordinate system during any series of measurements. This made it possible to take data as a function of the angle between the magnetic field and the current. The apparatus was aligned by rotating a germanium sample in the magnetic field and determining the position of parallel current and magnetic field from the zero of the germanium Hall voltage. For all measurements Ohmic contacts were made to the sample using pure tin solder. Standard dc potentiometric methods were used to measure voltages. Measurements were made at magnetic field intensities for which the weak-field approximation holds (i.e., for small Hall angle). The temperature region was usually 77° to 297°K.

Since $CdAs_2$ is tetragonal,[7] the resistivity and galvanomagnetic coefficients are tensor quantities which may have several independent components. The number of possible independent components is a function of the symmetry of the crystal and can be determined in the case of weak magnetic fields by expanding the resistivity tensor as a power series in $H$, the magnetic field. The resulting coefficients of the powers of $H$ are tensors, the form of which can be found by requiring invariance under operations with the crystal symmetry group.[8] In the case of $CdAs_2$ we can reduce the number of independent components of the Hall tensor to two, one occurring when $H$ is in the plane perpendicular to the fourfold symmetry axis and the second when $H$ is applied parallel to the fourfold symmetry axis.[8] We shall label these components of the Hall tensor $R_1$ and $R_3$.

Two experimental arrangements were used in investigating the Hall anisotropy. In the first a rectangular bar was cut along the crystallographic $a$ direction [Fig. 1(a)] and the Hall voltage measured with $H$ applied parallel and then perpendicular to the fourfold ($c$) symmetry axis ($H$ was always perpendicular to the current). Care was taken in each case to place the contacts in the same cross-sectional plane of the sample. In the second arrangement a rectangular bar was cut in the $b$-$c$ plane at 45° to the $c$ axis [Fig. 1(b)] and the magnetic field rotated about an axis perpendicular to the plane. It can be shown[9] that the maximum in the sine curve generated by the Hall voltage as a function of the angle between $H$ and the current will occur at an angle $\theta$ when $\tan\theta=(R_3+R_1)/(R_3-R_1)$.

Samples on which detailed measurements were made were cut from pulled single-crystal material prepared by a modified Gremmelmaier technique.[2] Care was

[1] V. J. Lyons and V. J. Silvestri, J. Phys. Chem. **64**, 266 (1960).
[2] G. A. Silvey, V. J. Lyons, and V. J. Silvestri (to be published). This work contains extensive references on the preparation of II–V compounds.
[3] W. J. Turner, A. S. Fischler, and W. E. Reese, J. Electrochem. Soc. **106**, 206c (1959).
[4] W. J. Turner, A. S. Fischler, and W. E. Reese, (Phys. Rev. **121**, 759 1961).
[5] M. J. Stevenson, Phys. Rev. Letters **3**, 464 (1959).
[6] M. J. Stevenson, Proceedings of the International Semiconductor Conference, Prague, 1960 (to be published).
[7] M. E. Senko and N. R. Stemple, Acta. Cryst. (to be published).
[8] T. Okada, Mem. Fac. Sci. Kyusyu Univ. Ser. B **1**, 157 (1955).
[9] For the orientation of Fig. 1(b) the Hall field $E_H$ as a function of the angle $\theta$, between $H$ and the current density $I$, is given as

$$2E_H/IH=(R_3-R_1)\cos\theta-(R_3+R_1)\sin\theta.$$

Upon differentiation with respect to $\theta$, the maxima of the expression are found to occur at $\tan\theta=(R_3+R_1)/(R_3-R_1)$.

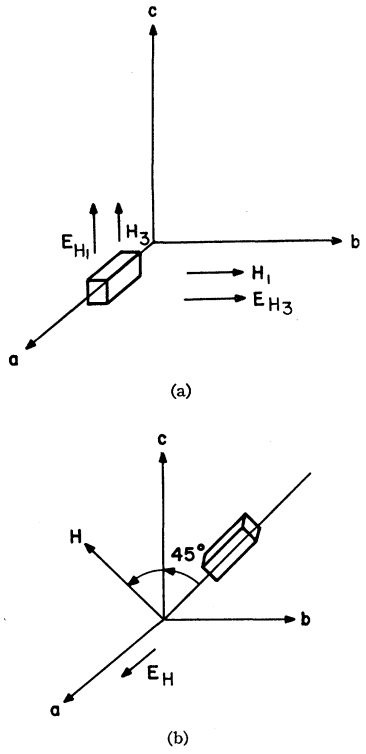



FIG. 1. Schematics of experiments to determine Hall anisotropy. (a) An $a$-directed sample with $H$ applied parallel to the equivalent $b$ axis or the fourfold $c$ axis. $E_{H3}$ is the Hall field associated with $R_3$ and $E_{H1}$ that associated with $R_1$. (b) A sample cut at 45° to the $c$ axis in the $b$-$c$ plane. The magnetic field is rotated about the $a$ axis, while the Hall is voltage measured parallel to the $a$ axis.

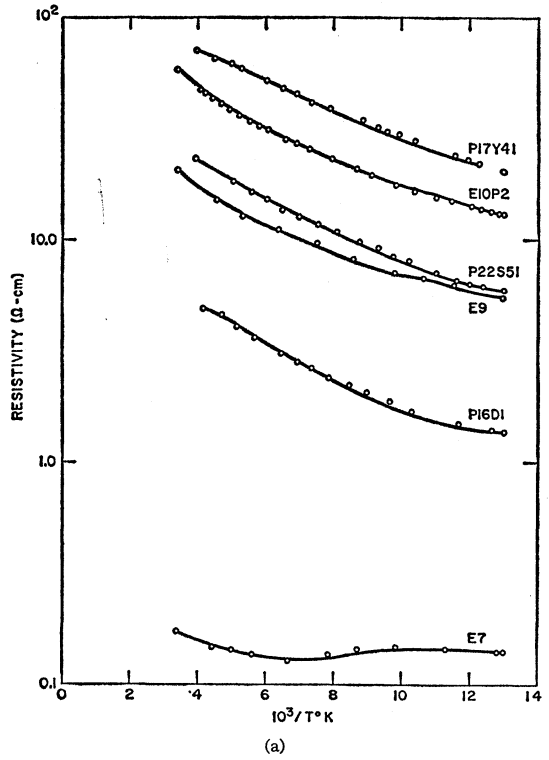
exercised in selecting samples that were homogeneous. Samples cut far from the growth axis of a rapidly pulled ingot often exhibited spurious effects,[10] the magnitude of which depended upon the growth rate of the crystal and the position from which the sample was cut. These results were incorrectly interpreted in reference 10. Similar spurious behavior has recently

TABLE I. Orientations, spectrographic impurities, and measured values of the Hall coefficients and resistivities of all samples at 77° and 250°K.

| Sample | Orientations | Spectroscopically determined impurities | Hall coefficient ($cm^3$/coul) 77° | Resistivity (ohm cm) 77°K | Hall coefficient ($cm^3$/coul) 250°K | Resistivity (ohm cm) 250°K |
|---|---|---|---|---|---|---|
| *E7* | | | 35 | 0.14 | 29 | 0.16 |
| *E9* | | | 730 | 5.45 | 630 | 18.0 |
| *E10P2C* | *c* | Mg | 6650 | 3.0 | 5300 | 12.4 |
| *E10P2A* | *a* | Mg | 6600 | 13.0 | 5000 | 49.0 |
| *P16D1* | *c* | Si, Cu, Pb | 2200 | 1.38 | 1700 | 5.4 |
| *P16SC*[a] | | Si, Cu, Pb | 36 000 | 35.0 | | 146.0 |
| *P17Y41* | *a* | None | 15 000 | 20 | 10 200 | 70.0 |
| *P18Z12* | *a* | Pb | 23 900 | 61 | | |
| *P21X3* | *c* | None | 4040 | 1.11 | 3180 | 5.2 |
| *P21X13* | *a* | None | 6250 | 6.7 | 5300 | 29.0 |
| *P21X14* | *a* | None | 7600 | 12.5 | 6000 | 50.5 |
| *P22S11* | *a* | None | 3900 | 5.60 | 3050 | 22.0 |
| *P22S12* | *a* | None | 4750 | 5.82 | 3650 | 22.5 |
| *P22S14* | *a* | None | 5940 | 12.15 | 4400 | 46.0 |
| *P22S51* | *c* | None | 10 960 | 5.87 | 9800 | 23.2 |

[a] This sample was cut in the $b$-$c$ plane at 45° to the $c$ axis.

[10] A. S. Fischler, Bull. Am. Phys. Soc. **5**, 77 (1960).



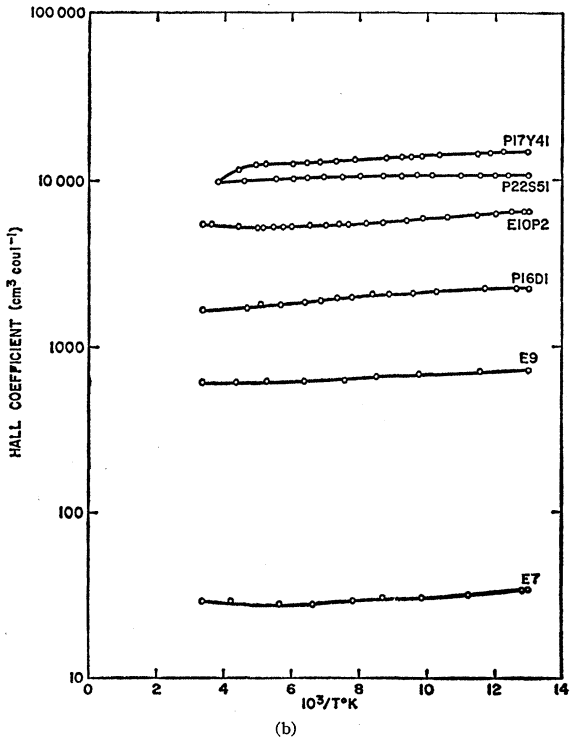




FIG. 2. Resistivity [Fig. 2(a)] and Hall coefficient [Fig. 2(b)] versus $10^3/T$ for several samples of $n$-type $CdAs_2$.

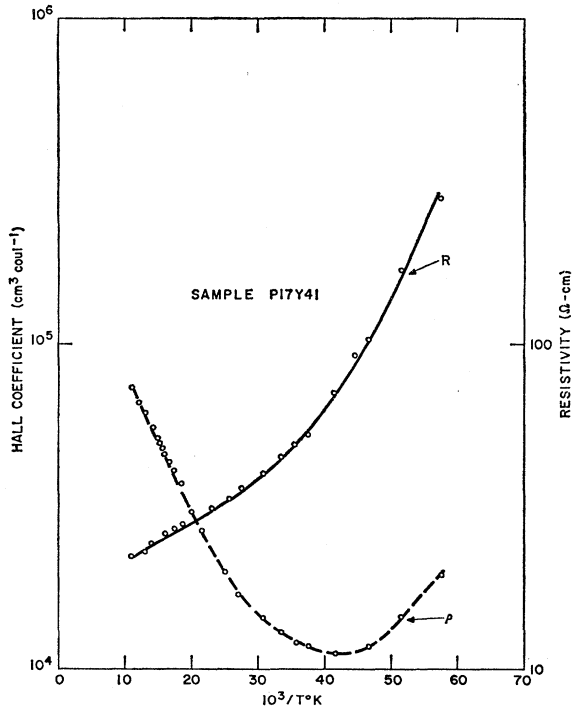



FIG. 3. Hall coefficient (smooth line) and resistivity (dashed line) extended to lower temperatures for a typical sample.

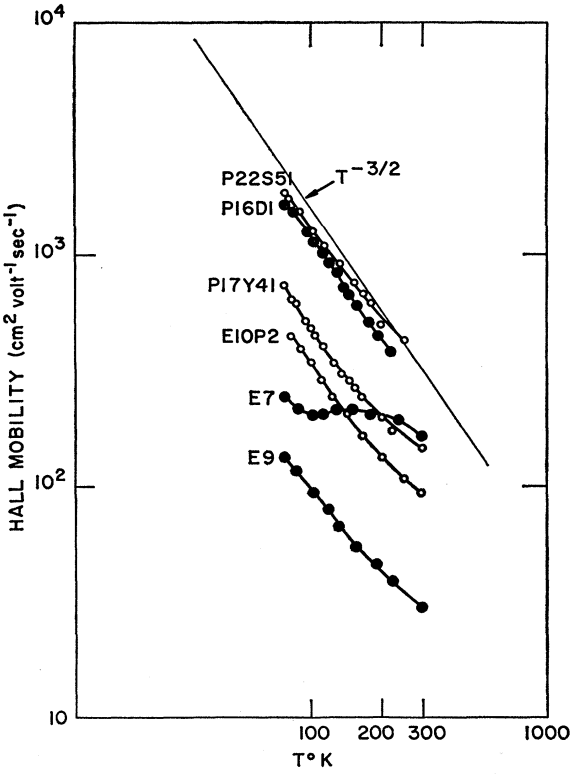



FIG. 4. Hall mobility, $R/\rho$, versus absolute temperature for the samples of Fig. 2. The line of slope $-\frac{3}{2}$ is included for reference.

been observed in InSb.[11] To minimize these effects, crystals were pulled slowly (about 0.25 cm per hr) and samples cut from positions near the growth axis.

## II. RESULTS

### (a) Energy Gap

Optical energy gap values have previously been reported.[3,4] These show a slight directional dependence of the absorption edge and give an average value of $\Delta E=1.02$ ev for the energy gap at room temperature. Because the compound is thermally unstable at temperatures in excess of 400°K, no extensive study of the intrinsic properties was undertaken. However, an energy gap value was obtained from high-temperature resistivity data giving a value of $\Delta E=1.13$ ev when extrapolated to absolute zero.

### (b) Resistivity, Hall Coefficient, and Hall Mobility vs Temperature

The resistivity, $\rho$, and Hall coefficients of typical samples of $n$-type $CdAs_2$ are shown as a function of reciprocal temperature (Fig. 2). Curves of several other samples measured fell in the same resistivity range as those of Fig. 2 and are not reproduced. Table I provides data on all samples measured. Samples $E$-7 and $E$-9 were unoriented, boat grown, single-crystal samples. All others were cut from pulled single-crystal material. Orientations and spectroscopically determined impurities are given in columns 2 and 3 of Table I. Figure 3 shows an extension of the data of Fig. 2 to lower temperatures for a typical sample. The resistivity minima, due to carrier freeze-out, occurred at about 25°K in the two samples measured. The measurements were not extended to low enough temperatures to allow determination of impurity activation energies. Above 50°K the variation in $R_1$ and $R_3$ is associated with the variation in the Hall to conductivity mobility ratio with temperature. The Hall mobility, $R/\rho$ (Fig. 4) is a decreasing function of temperature indicating the scattering to be predominantly by lattice modes.

### (c) Investigation of Hall Anisotropy

Measurements on $a$-direction samples as outlined in Sec. II gave values of $R_1/R_3=0.98\pm0.05$ where the error results from variations in sample cross section. The Hall coefficient of a sample cut as shown in Fig. 1(b) with the magnetic field rotated about the $a$ axis generated the curve of Fig. 5. The slight shift in the maximum of the Hall voltage is within the experimental error. Therefore, from these measurements we can conclude that the Hall coefficient shows no discernible anisotropy.

[11] H. Rupprect, R. Weber, and H. Weiss (to be published).

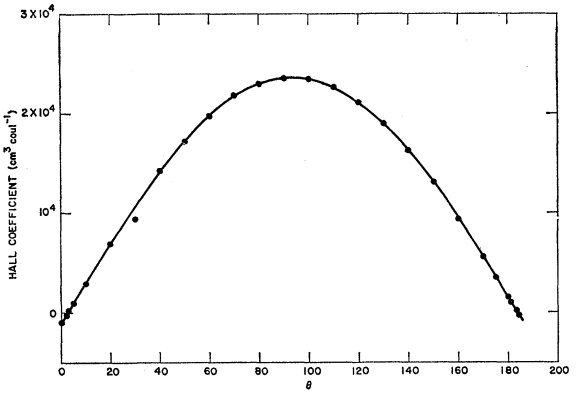



FIG. 5. Curve of Hall coefficient versus angle between the current and magnetic field for a sample oriented as shown in Fig. 1(b). The data were taken at 77°K with a magnetic field of 6800 gauss.

### (d) Magnetoresistance

Figure 6 shows the results of magnetoresistance measurements made on a $c$-direction sample at 77°K. The solid line represents the curve $\Delta\rho/\rho=12.5\times10^{-3}\times\sin^2\theta$. The longitudinal magnetoresistance was always less than 5% of the transverse for $c$-direction samples. The mobility calculated from magnetoresistance, assuming lattice scattering, was in agreement with the mobility obtained from Hall and resistivity data.

For $a$-directed samples transverse magnetoresistance with $H$ perpendicular to the $c$ axis was always greater than with $H$ parallel to the $c$ axis. The ratios of transverse magnetoresistances were between 2.2 and 4.2 for all samples measured.

## III. DISCUSSION

The data presented in the previous section can be interpreted in terms of a simple energy-band model, namely ellipsoidal energy surfaces with axes of rotation parallel to the $c$ axis of the crystal. This model of the energy band structure is consistent with the requirements of crystal symmetry if the energy minima lie on the $c$ axis in momentum space. There are two possibilities, either a single conduction-band minimum at $k=0$ or two minima located at equivalent points along $k_z$. These models are indistinguishable in terms of the present experiment. The important features of the galvanomagnetic effects which establish the above model are the independence of the Hall coefficient on direction and the near absence of longitudinal magnetoresistance. These results are in agreement with cyclotron resonance data.[5,6]

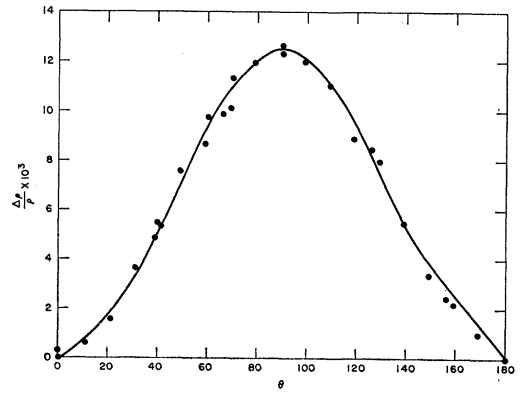



FIG. 6. Magnetoresistance of a $c$-directed sample versus the angle between the current and magnetic field. The solid line is the curve $\Delta\rho/\rho=12.5\times10^{-3}\sin^2\theta$. The data were taken at 77°K with a magnetic field of 14 000 gauss.

Values of the anisotropy ratio $K=\tau_{\parallel}m_{\perp}/\tau_{\perp}m_{\parallel}$ can be obtained by comparison of the resistivity ratio $\rho_{\perp}/\rho_{\parallel}$ where the subscripts refer to quantities perpendicular and parallel to the fourfold symmetry axis. This ratio can be determined by comparing resistivity data of samples cut along different axes, but grown under identical conditions, with similar carrier concentrations, e.g., $E10P2A$, $E10P2C$ of Table I. Where the carrier densities of two similarly prepared samples did not differ by more than 20%, the resistivities were adjusted to an average carrier concentration and the values of $K$ calculated from the adjusted values. The anisotropy ratios computed from several pairs of samples at various temperatures are listed in Table II.

TABLE II. Values of $K=\tau_{\parallel}m_{\perp}/\tau_{\perp}m_{\parallel}$ determined at several temperatures. The latest value of $m_{\perp}/m_{\parallel}$ obtained by Stevenson[a] from cyclotron resonance measurements is given in the last column.

| Samples | $K=\tau_{\parallel}m_{\perp}/\tau_{\perp}m_{\parallel}$[b] 77°K | 125°K | 200°K | 250°K | $m_{\perp}/m_{\parallel}$ |
|---|---|---|---|---|---|
| $E10P2A$, $E10P2C$ | 4.30 | 4.02 | 3.85 | 3.72 | |
| $P22S11$, $P21X3$ | 5.27 | 4.63 | 4.43 | 4.41 | 3.87 |
| $P22S12$, $P21X3$ | 4.44 | 3.95 | 3.83 | 3.78 | |

[a] See reference 6.
[b] The absolute values of $K$ are accurate to $\pm0.05$. The values of $K$ as a function of temperature depend on the relative values of the resistivity measurements and are accurate to $\pm0.01$. Therefore, the $K$ values are recorded to three significant figures.

The variation of $K$ with temperature is a consequence of the decrease in ionized impurity scattering with temperature. At high temperatures $K$ should approach a limiting value associated with pure lattice scattering. The results indicate that this value is close to the cyclotron resonance effective-mass ratio (last column, Table II) and suggest isotropic, energy-dependent, relaxation times. Herring[12] has pointed out that for nonspherical energy surfaces and acoustical mode scattering, the assumption of an energy-dependent relaxation time improves as the mass anisotropy increases. It is of interest that the current work implies this may be true for anisotropies as small as four.

[12] C. Herring, Bell System Tech. J. 34, 237 (1955).

## CONCLUSION

Experimental data obtained on samples of $n$-type $CdAs_2$ have been fitted to a simple energy-band model consisting of either a single conduction-band minimum at $k=0$ or two minima located at equivalent points along $k_z$. This is in agreement with cyclotron resonance observations. Values of the anisotropy constant $K=\tau_{\parallel}m_{\perp}/\tau_{\perp}m_{\parallel}$ were obtained from Hall and resistivity data and indicate that $\tau_{\parallel}/\tau_{\perp}$ is approximately unity above 250°K.

## ACKNOWLEDGMENTS

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# Nuclear Quadrupole Resonance in an Antiferromagnet

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Nuclear quadrupole resonance techniques have been used to investigate magnetic interactions in the bromates and iodates of certain 3$d$ transition metal ions. In particular, for $Ni(IO_3)_2\cdot 2H_2O$ there is an abrupt disappearance of the $I^{127}(\pm 3/2 \leftrightarrow \pm 1/2)$ transition at 3.08°K; at lower temperatures there is a large, temperature-dependent splitting. This behavior is attributed to the combined effects of an antiferromagnetic ordering of the $Ni^{++}$ electron spins and a hfs interaction of the nonlocalized $Ni^{++}$ spin magnetization with the $I^{127}$ nuclear magnetic moment. Measurements of the pure quadrupole transition frequencies above, and of their temperature-dependent splittings below, the Néel temperature yield the quadrupole coupling constant, the asymmetry of the electric field gradient (EFG) tensor, the magnitude and orientation of the internal magnetic field relative to the principal axes of the EFG tensor, and the sublattice magnetization as a function of temperature. Qualitative experiments at 1.3°K indicate $T_1^{127}\ll 100$ sec and $T_2^{127}\sim 10^{-6}$ sec. Measurements of the rf and dc magnetic susceptibility have been made and are consistent with these conclusions and, in addition, indicate the sudden onset of a spontaneous ferromagnetic moment as the temperature is lowered below $T_n$. A possible isotope effect on the $T_n$ of $Ni(IO_3)\cdot 2H_2O$ was looked for but none was found. Cupric iodate and the bromates give no evidence of magnetic ordering above 1.3°K.

## INTRODUCTION

WE present in the following the results of observations of nuclear quadrupole resonance in an antiferromagnet.[1] Since this constitutes the first such observation, we briefly review nuclear resonance phenomena in antiferromagnets.

In recent years the techniques of nuclear magnetic resonance (NMR) have been successfully applied to the study of local fields in magnetic solids both in the paramagnetic and ordered states. If, in addition, a nucleus possesses an electric quadrupole moment $Q$, and is subject to an electric field gradient (EFG), resonances may be observable without an external magnetic field, either in single crystals or in polycrystalline samples. These so called "pure quadrupole resonances" we denote by NQR. Aside from the experimental convenience, observation of the quadrupole transitions permits a comparison of the directions of the EFG tensor and internal magnetic field in an ordered magnetic material.

Before discussing the effects that result from combined nuclear magnetic moment and nuclear electric quadrupole moment interactions, it is perhaps instructive to briefly classify the nuclei according to their electronic environments and their possible electric and magnetic interactions. (We restrict our discussion to insulating magnetic solids.)

*Magnetic interactions.* (1) Nuclei of paramagnetic ions (e.g., $Co^{59}$ in $CoF_2$).[2] The nucleus is immersed in large hyperfine fields arising from the magnetic electrons of *its own* ion in addition to the dipolar fields of all other magnetic ions.

(2) Nuclei of nominally diamagnetic ions (e.g., $F^{19}$ in $CoF_2$).[3] If an appreciable overlap exists between the

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[1] A preliminary report of this work was given at the November, 1959 American Physical Society Meeting [J. C. Burgiel, V. Jaccarino, and A. L. Schawlow, Bull. Am. Phys. Soc. 4, 424 (1959)].

[2] V. Jaccarino, Phys. Rev. Letters 2, 163 (1959).

[3] V. Jaccarino, R. G. Shulman, and J. W. Stout, Phys. Rev. 106, 602 (1957).