irradiated KCl can very plausibly be attributed to optical pumping. Although they used unpolarized light, a net pumping effect can result because, as in Table II, the *p* factors for σ^+ and σ^- need not cancel.

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PURE NUCLEAR QUADRUPOLE RESONANCES IN PARAMAGNETIC IRON-GROUP HALIDES

R. G. Barnes and S. L. Segel
Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa*

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Although the number of compounds in which pure nuclear quadrupole resonances have been detected now runs into the hundreds, no resonance appears ever to have been reported in a paramagnetic substance. The observation, by Shulman and Jaccarino,[1] of the nuclear magnetic resonance of F^{19} in MnF_2 and some related paramagnetic compounds demonstrated that the nuclear resonance line width was not necessarily so broad as to preclude its detection. In fact, although the dipolar field of the Mn^{2+} ions in MnF_2 is very large and the hyperfine field due to the covalent bonding is even larger, both effects are swamped by the effective exchange field responsible for the antiferromagnetic ordering at 68°K. A detailed theoretical study by Moriya[2] of the relaxation processes in the antiferromagnetic and paramagnetic states anticipated the experimental findings. The same arguments might be expected to apply equally well in the pure quadrupole case. In spite of the large dipolar fields of the magnetic ions, the quadrupole resonances ought to be sufficiently exchange-narrowed to be observable if the substance has a large exchange energy (i.e., an ordering temperature greater than a few degrees K). Indeed, Jaccarino[3] has observed the quadrupole splitting of the nuclear magnetic resonance lines of Co^{59} in antiferromagnetic CoF_2.

A considerable number of iron-group chlorides and bromides are structurally identical to or very closely similar to the BiI_3 structure.[4] In this structure, the metal ions occur in layers between layers of close-packed halogens, such "sandwiches" being stacked to form the entire crystal. The layers of metal ions are thus separated by two halogen layers. Recent neutron diffraction work by the Oak Ridge group[5] has shown that these compounds become antiferromagnetic at appreciable temperatures, the ordering being with few exceptions ferromagnetic within the metal ion layer and with alternate layers arranged antiferromagnetically. Several diamagnetic compounds also utilize the BiI_3 structure, including AsI_3, SbI_3, and BiI_3 itself. The iodine nuclear quadrupole resonances in these compounds were reported some years ago[6]; the coupling constants appear to be consistent with the view that the bonding within the halogen-metal-halogen sandwich is largely covalent. The arsenic and antimony resonances have also been detected.[7] In consequence, it seemed reasonable to search for nuclear quadrupole resonances in some of the chlorides and bromides of the iron-group ele-

Table I. Nuclear quadrupole resonance frequencies of Cl^{35} and Br^{81} nuclei in iron-group halides.

Compound	ν_{res} at 24°C (Mc/sec)	Magnetic ordering temp. (°K)	Covalent character α^2
$TiCl_3$	7.39		0.27
$TiCl_2$	4.17		
VCl_3	9.40	30[a]	0.34
$CrCl_3$	12.812 12.848	17[b]	0.47
$CrBr_3$	85.73		0.53
$CrCl_2$	8.52	20[b]	

[a] Temperature of susceptibility maximum.
[b] Neutron diffraction value.

ments.

We have detected such resonances in polycrystalline samples of $TiCl_3$, $TiCl_2$, VCl_3, $CrCl_3$, $CrBr_3$, and $CrCl_2$. The observed Cl^{35} and Br^{81} resonance frequencies are listed in Table I. In all cases, the Cl^{37} and Br^{79} resonances were also detected to guarantee the isotopic assignment. The experimental apparatus consisted of a variety of superregenerative spectrometers; magnetic modulation and recording techniques were used in all cases, the resonances in $CrCl_3$ and $CrBr_3$ being the only ones observable with oscilloscope display. Figure 1 shows a portion of the Cl^{35} spectrum in $CrCl_3$. Two lines with an intensity ratio of 2:1 are observed, corresponding to crystallographically nonequivalent sites; the line widths are about 15 kc/sec. Attempts to record these resonances with a Pound-Watkins type regenerative spectrometer were unsuccessful, probably because of the poor performance of such spectrometers at higher rf power levels.

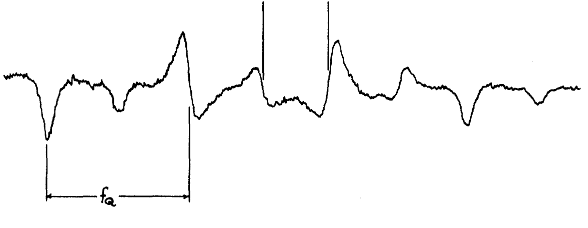

FIG. 1. Portion of superregenerative spectrometer tracing of Cl^{35} nuclear quadrupole resonance spectrum in $CrCl_3$. The quench frequency is 70 kc/sec.

Table I also lists the magnetic ordering temperature for those substances for which it is known. That resonances have been detected in some compounds for which ordering temperatures have not been determined suggests that the ordering temperatures of these compounds are also appreciable. In the case of $CrCl_3$, the resonance in the powdered sample was undetected at 4.2°K, but as the temperature was allowed to rise, the resonance appeared abruptly in the vicinity of 17°K. The large internal fields in the antiferromagnetic state give rise to a nuclear Zeeman energy which is at least comparable to the nuclear quadrupole energy, thereby rendering the resonance unobservable in the powdered sample.

The quadrupole resonance frequencies provide an estimate of the covalent character α^2 of the metal-halogen bond in these compounds. In the trihalides, the halogen coupling constant on a simple valence-bond model is given approximately by

$$eQq_{\text{obs}} = \tfrac{1}{2}\alpha^2 eQq_{zz}, \tag{1}$$

where eQq_{zz} is the coupling constant for one unbalanced p-electron.

Values of α^2 calculated from (1) are also listed in Table I. They are in reasonable agreement with estimates based on the electronegativities of the atoms.[8] Considerations of s-hybridization and the weak bonding between adjacent halogen layers would modify these results somewhat. In the dihalides, eQq_{obs} depends very sensitively on the interbond angle θ at the halogen, which is about 89° in these compounds, so that the determination of α^2 is less reliable.

The covalent character may be related to the admixture coefficient λ of molecular orbital theory. Stevens[9] and Owen[10] have studied the effect of magnetic electron transfer on various ionic properties, and Owen[10] has estimated that the fractional importance of the anion $3d_\gamma$ orbitals in σ-bonding for Cr^{3+} in the chromium hexahydrate ion is given by $\lambda^2 \approx 0.7$. This may be compared with $\lambda^2 = 0.76$ for Cr^{3+} in $CrCl_3$ based on the Cl^{35} quadrupole coupling constant. Both results indicate considerable participation of the empty $3d_\gamma$ orbitals in σ-bonding. On the other hand, the fact that the F^{19} resonance in CrF_3 is virtually unshifted,[11] implies that the $3d_\epsilon{}^3$ configuration participates negligibly in covalent bonding.

The study of the magnetic resonance spectra of both the cation and anion nuclei in a single crystal ought to be especially fruitful. In this way, a determination of the electric field gradient and magnetic hyperfine tensors at all nuclei in the crystal would be obtained. A complete analysis of covalent bonding structures could then be made.[12]

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CYCLOTRON RESONANCE IN CdAs$_2$

Mirek J. Stevenson
Research Laboratory, International Business Machines Corporation, Poughkeepsie, New York

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Cyclotron resonance in nonmetals has been observed previously only in Ge,[1] Si,[2] InSb,[3] and recently in CdS.[4] Of these compounds only InSb was an intermetallic semiconductor, belonging to the III-V group of compounds. This Letter reports the first observation of cyclotron resonance in a II-V semiconductor, CdAs$_2$.

The crystals of CdAs$_2$ were grown from cadmium and arsenic of 99.999+% purity.[5] The crystals were spectrographically pure and x-ray analysis established them as single crystals of CdAs$_2$. Two disk-shaped n-type samples, 3 mm in diameter and about 0.6 mm thick, were used in the experiments reported here. The plane of the disk was perpendicular to the c axis for one sample and to the a axis for the second sample. All of the data were taken at frequencies between 20 000 Mc/sec and 24 000 Mc/sec and at temperatures below 2°K.

Figure 1 shows a typical plot of microwave absorption *versus* the magnetic field. Two absorption lines were resolved at all orientations. The higher field (higher effective mass) absorption line was identified with electrons by observation of microwave impact ionization and by excitation of carriers only from donor levels with filtered infrared radiation. When a Ge filter was used to eliminate light of energies sufficient to excite carriers across the 1.1-ev energy gap of CdAs$_2$, only the higher field (higher effective mass) resonance was observed at a diminished

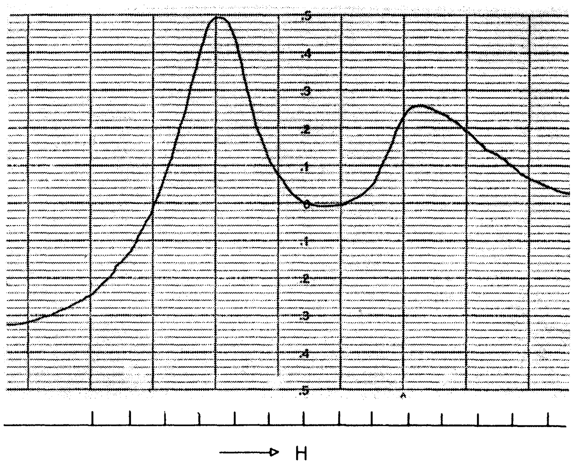

FIG. 1. Typical recording of power absorption as a function of magnetic field at a frequency of 20 835 Mc/sec and temperature below 2°K. The low-field line is identified with holes and the higher-field line with electrons.

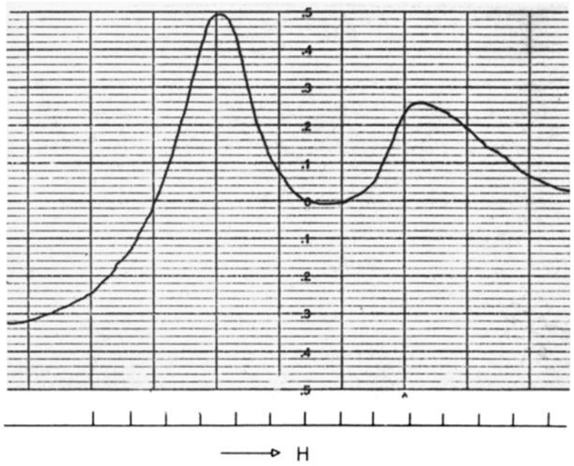

FIG. 1. Typical recording of power absorption as a function of magnetic field at a frequency of 20 835 Mc/sec and temperature below 2°K. The low-field line is identified with holes and the higher-field line with electrons.