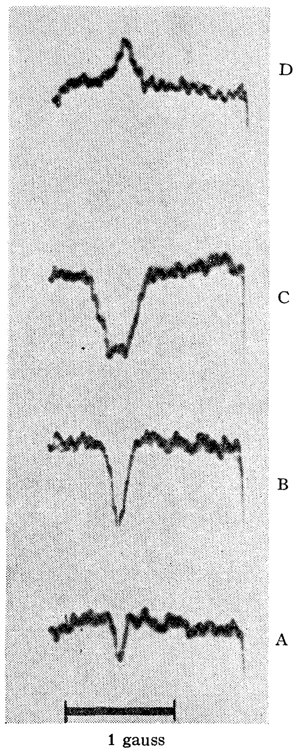

FIG. 2. Oscilloscope traces of $\lambda 5461$ absorption by $^3P_2$ mercury atoms *versus* field H_0. A shows the decrease in absorption by paramagnetic resonance reorientation induced by a rf field of ~12.5 milligauss, B and C are for ~62.5 and ~250 milligauss. Radiation polarized parallel to H_0 was employed for $A-C$. D shows the increase in absorption when polarization perpendicular to H_0 was used; rf field ~62.5 milligauss.

Two weaker resonances corresponding to the $F=3/2$, $5/2$ states for the Hg^{199} isotope have also been observed at the expected field values. The extensions of the method to observe $\Delta F=\pm 1$ transitions for the odd isotopes which would allow a precision determination of the hfs are obvious.

The author wishes to express his appreciation to his colleagues for advice and equipment, and to Mr. D. A. Schow and Mr. J. Jonson for the construction of the potassium resonance equipment and of various excitation tubes, respectively.

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Ferroelectricity in the Langbeinite System*

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OPTICAL examination of $(NH_4)_2Cd_2(SO_4)_3$ over the range from room temperature to 77°K revealed a crystal transition about 10° above the lowest temperature. The material is cubic above the transition point, and belongs to the Langbeinite $[K_2Mg_2(SO_4)_3]$ family. An x-ray powder pattern establishes the lattice constant as $a=10.35_0\pm 0.005$ A. Growth from water solution at 80°C results in predominance of octahedral (111) faces.

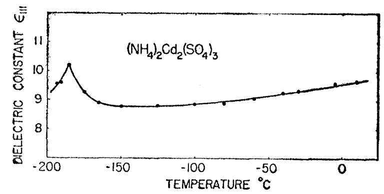

FIG. 1. Dielectric constant of $(NH_4)_2Cd_2(SO_4)_3$ as function of temperature, measured along cubic [111] direction.

Dielectric measurements were made on plates cut perpendicular to the cubic [111] direction. The behavior of the low-field dielectric constant ϵ_{111} as a function of temperature is depicted in Fig. 1. The room-temperature value of ϵ_{111} is about 9.5; the constant begins to climb slightly at -160°C, and reaches a peak of 10.2 at -184°C. Below this point, ferroelectric hysteresis loops are observed. The coercive field at -190°C is approximately 15 kv/cm for an applied field of 25 kv/cm, and the spontaneous polarization above the former [111] cube direction is about 0.3 microcoulomb/cm^2. The hysteresis loops sometimes appear with noncentric symmetry, as in the case of guanidinium aluminum sulfate hexahydrate as reported by Holden *et al.*[1]

Detailed dielectric, optical, thermal, and x-ray measurements on this and isomorphous crystals are in progress.

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Effects of Superexchange on the Nuclear Magnetic Resonance of MnF_2

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NUCLEAR magnetic resonances of F^{19} in oriented single crystals of MnF_2 have been observed at 77°K, 195°K, and 310°K. Two broad F^{19} resonances were found (corresponding to the two nonequivalent fluorine sites in the unit cell) whose separation shift from the F^{19} resonance in a diamagnetic material, were functions of the external magnetic field, crystal orientation, and temperature.

Bloembergen and Poulis[1] have pointed out that for crystal orientations such that H_0 is contained in the a-b plane, two F^{19} resonances are to be expected while only one is to be found for H_0 in the b-c plane. With the former orientation we have observed the separate lines at 77°K, while at 310°K the lines were not resolved.

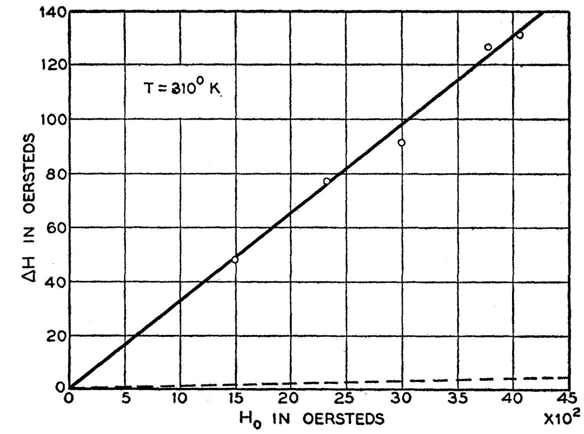

FIG. 1. The shift in the F^{19} resonance field from $\omega/\gamma_{F^{19}}$ *vs* the external magnetic field. The dotted curve represents the predicted paramagnetic shift when H_0 is parallel to the b axis and is given by Eq. (1).

At 310°K, with $H_0 \perp b$, a line was observed which differed from ω/γ_F by an amount we designate by ΔH; ΔH is plotted *vs* H_0 in Fig. 1. It is to be noticed that ΔH is proportional to H_0 and is ~30 times larger than the "paramagnetic shift" expected. The "paramagnetic shift" arises from the time averaged magnetic field at the F^{19} position due to the paramagnetic Mn^{++} ions. Its magnitude for temperatures greater than the transition temperature can be shown to be

$$\Delta H_i \simeq \frac{g^2\beta^2 H_0 S(S+1)}{3k(T+\Theta)} \sum_i \frac{(1-3\cos^2\theta_{ij})}{r_{ij}^3}, \qquad (1)$$

where the summation is over the Mn^{++} sites, θ_{ij} is the angle between r_{ij} and H_0 and the other symbols are conventional. In addition, ΔH depended upon the temperature. The experimental values are, for 15.33 Mc/sec: $T=310$°K, $\Delta H=118$ oe; $T=195$°K, $\Delta H=150$ oe; $T=77$°K, $\Delta H=257$ oe. These values roughly agree with the temperature dependence of Eq. (1).

In Fig. 2 the measured separation of the two resolved lines is plotted as a function of the angle between H_0 and the b axis at 15.33 Mc/sec and 77°K. There is

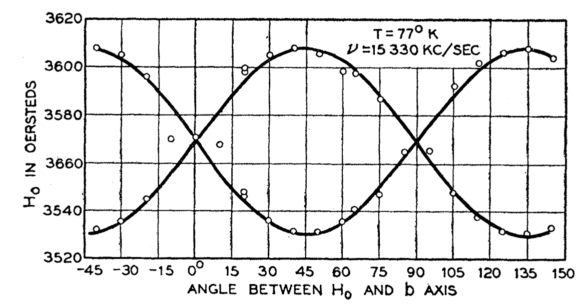

FIG. 2. Resonant magnetic field for F^{19} nuclei *vs* angle between H_0 and the b axis with H_0 in the a-b plane. The theoretical angular dependence including contributions from near neighbors only is indicated, normalized to the amplitudes of the experimental data at $\Phi=45°$.

plotted as well (solid line) the theoretical angular dependence, where we have only included contributions from the three nearest Mn^{++} normalized to a best fit with the experimental points. From the paramagnetic shift at this field and temperature, one calculates an extreme splitting of 60 oe and an average displacement of 7 oe from ω/γ_F. These values are to be compared with the observed extreme splitting of 77 oe and the observed mean shift of 277 oe, when we include the demagnetizing correction for our spherical sample.

When the lines were resolved it was possible to determine that they were Lorentzian in shape. In addition, the signal-to-noise ratio was directly proportional to H_1 indicating that $(\gamma H_1)^2 T_1 T_2 \ll 1$. This suggests that the observed line widths of the resolved lines (28.5 oe peak to peak of the derivative curve) arise from uncertainty broadening and that $T_1 = T_2 = 1.6 \times 10^{-6}$ sec at 77°K. The unresolved line widths at 310°K are consistent with this value. Considering the line widths to be determined by the observed hyperfine interaction and exchange narrowing, one can calculate $T_1 \sim 2 \times 10^{-6}$ sec.

At 68°K, corresponding to the antiferromagnetic transition temperature, the lines disappear.

The most reasonable explanation of the large shift is to suppose that an electron of the closed fluorine shell is promoted to the Mn^{++} ion and that the F^{19} nucleus is immersed in the large magnetic field of its own unpaired electrons for some part of the time. The magnitude of this field may be estimated from the calculated $\psi^2(0)$ for an s electron. The fraction of the time that the electron is unpaired can then be calculated to be 2.5%. This promotion of the fluorine electron is the superexchange[2] mechanism and we see that nuclear magnetic resonance can provide a direct measure of superexchange.

We should like to thank P. W. Anderson for stimulating discussions about the applicability of superexchange, B. J. Wyluda for experimental assistance, E. F. Dearborn for growing the crystals, and J. F, Dillon, Jr., for helping to prepare samples.

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Nuclear Magnetic Resonance of Si^{29} in n- and p-Type Silicon

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WE have observed the nuclear magnetic resonances of Si^{29} in high purity silicon at room temperature and have determined the spin-lattice relaxation time as a function of sample resistivity. The resonance lines were observed with a Varian Associates variable-