

larger than that to be expected from the dipole field of the Mn^{2+} ions. As in the work of Tinkham^{9,10} on the electron spin resonance of the manganese ion in ZnF_2 , they found⁷ that the nondipolar parts of the shifts of the observed F^{19} lines could be accounted for by means of a tensor hyperfine interaction between the time average spin $\langle \mathbf{S}_j \rangle$ of the manganese neighbors, and the nuclear spin I of the fluorine in the form $\mathbf{I} \cdot \sum_j \mathbf{A}_j \cdot \langle \mathbf{S}_j \rangle$. In order to explain the presence of this hyperfine interaction tensor they proposed that the nominally paired spins on the fluorines were slightly unpaired because of an admixture of covalent bonding into the purely ionic configuration.

By studies of the temperature dependence of the F^{19} resonance frequency in the antiferromagnetic region, Jaccarino¹¹ and Walker were able to obtain extremely accurate measurements of the temperature dependence of the sublattice magnetization $M(T)$. Furthermore, Jaccarino et al. found¹² that below T_N the nuclear resonance could not be observed in precipitated powders of MnF_2 . In order to determine if this resulted from a distribution of large internal strains in each of the crystallites Jaccarino et al.¹² subjected a single crystal of MnF_2 to a uniaxial stress and showed that the resonance frequency was indeed a strong function of the stress.

In previous papers we have shown the usefulness of high-pressure measurements in elucidating in detail the electric field gradients in nonconducting crystals,¹³ and

the hyperfine interaction between the conduction electrons and the nuclei in the alkali metals and copper.¹⁴ High-pressure experiments are a powerful aid to the theory because they provide a means of continually varying the lattice parameters which stand on an equal footing with the temperature in the theoretical description of the state of the solid. Thus, soon after Jaccarino and Shulman's observation of the nuclear resonance in antiferromagnetic MnF_2 , the present study was begun in the hope of gaining some insight into the detailed nature of the coupling between the magnetic electrons and the fluorine nuclei. The antiferromagnetic region is especially suitable for these measurements because of the narrowness of the resonance line ($\Delta\nu \sim 50$ kc/sec), compared to the zero field resonance frequency ($\nu \sim 160$ Mc/sec).

From measurements of the pressure dependence of the resonance frequency at 4.2°K, 20.4°K, and 35.7°K, we have deduced the pressure dependence of the Néel temperature T_N , and the hyperfine interaction constant A . By combining this with our measurements of the compressibility of MnF_2 , we can determine the dependence of these quantities on the lattice parameters. Finally, we apply the theory of Mukherji and Das,¹⁵ and W. Marshall and R. N. Stuart¹⁶ to the calculation of the magnitude and pressure dependence of the hyperfine interaction constant. This theory represents a new theoretical treatment of the unpairing of spins on the fluorine and enables a straightforward calculation of the degree of this unpairing for all (n,l) groups in the fluorine ion. Agreement of this theory with the experimental results is most satisfactory.

II. EXPERIMENTAL METHODS AND RESULTS

1. Experimental Methods

The present experiment requires: a sensitive spectrometer capable of reproducing faithfully the line shape of the nuclear resonance in the difficult frequency region around 160 Mc/sec, while the sample is inside a high pressure bomb which is maintained at a rather low temperature ($4.2^\circ\text{K} \leq T \leq 36^\circ\text{K}$), a considerable distance (80–90 cm) from the spectrometer. Thus the experimental arrangement consists of three interrelated parts: (1) spectrometer, (2) high-pressure bomb and gas press, and (3) low-temperature system.

By far the most serious experimental difficulty was the vhf spectrometer. When this work was begun, no spectrometer was available which was flexible enough to satisfy our needs. This difficulty was overcome by the invention by one of us (T.K.), of a variable frequency vhf spectrometer, which possesses high sensitivity and good frequency stability. Figure 3 shows this spectrometer. The 6J6 oscillator operates push-pull

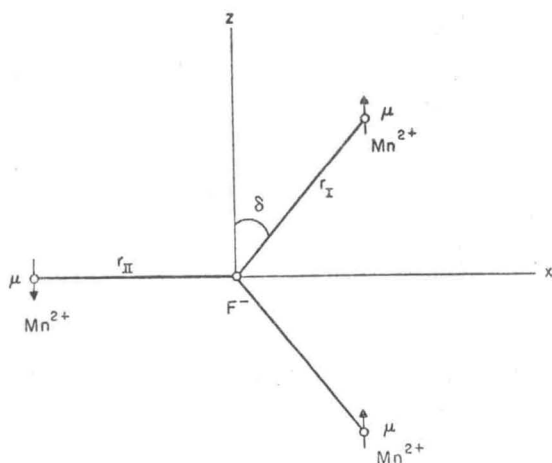


FIG. 2. The arrangement of nearest neighbor Mn^{2+} ions around a fluorine nucleus. The arrows represent the magnitude and relative orientation of the time averaged magnetic moment of the Mn^{2+} ions. A second type fluorine site sees the same configuration as above except that the direction of the Mn spins are reversed.

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