reasonable agreement with experiment and which might be brought considerably closer to experiment by a slight modification of the potential. We have also found that these results are close to self-consistency in the context of one modified HFS approximation ($A=0.7$, $B=0.71$) and far from self-consistency in another ($A=1.0$, $B=0.5$). On the other hand, the unmodified HFS approximation leads to a total spin per unit cell which is clearly too large. In contrast with the spin density, the calculated charge density has not shown sufficient sensitivity to the differences between potentials used in our calculations to account for the discrepancy in the x-ray scattering intensities.

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PHYSICAL REVIEW VOLUME 162, NUMBER 2 10 OCTOBER 1967

ac Magnetic Susceptibility and H-T Phase Diagram of $MnCl_2 \cdot 4H_2O$ between 0.26 and 1.50°K in Fields up to 27 kOe*

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The field-induced magnetic phase transitions in $MnCl_2 \cdot 4H_2O$ were investigated by measuring the differential magnetic susceptibility between 0.26 and 1.5°K in external magnetic fields up to 27 kOe. With the external field along the most preferred axis of the crystal (c' direction), both the antiferromagnetic–to–spin-flop (AF-to-SP) and the spin-flop–to–paramagnetic (SF-to-P) transitions were observed below 1.3°K. The AF-to-SF transition appears to be a first-order transition, as predicted by molecular-field theory. The temperature dependence of the phase boundary is given by $H_c=H_{c0}+bT$, where $H_{c0}=7550\pm10$ Oe and $b=434\pm10$ Oe/deg. Within the spin-flop state $\chi_{c'}$ is roughly constant and approximately equal to the value of $\chi_\perp$ in zero field. At the SF-to-P phase boundary, $\chi_{c'}$ drops rapidly to zero. The temperature dependence of the SF-to-P transition is given by $H_c=H_{c0}(1-CT^n)$ up to about 0.7°K, where $\mathrm{H}_{c0}=20.6\pm0.03$ kOe, $n=1.82\pm0.10$, and $c=0.228\pm0.002$.

MEASUREMENTS of the ac magnetic susceptibility of antiferromagnetic $MnCl_2 \cdot 4H_2O$ have been made in fields up to 27 kOe in the temperature range 0.26 to 1.5°K. Both the antiferromagnetic–to–spin-flop (AF-to-SF) and the spin-flop–to–paramagnetic (SF-to-P) phase transition boundaries were clearly determined from the data. These two phase boundaries together with the antiferromagnetic-to-paramagnetic (AF-to-P) boundary form a triple point at 1.30°K. The AF-to-SF critical field was found to fit the equation H_c (AF-to-SF) $=H_{c0}+bT$, where $H_{c0}=7550\pm10$ Oe and $b=434\pm10$ Oe/deg throughout the entire temperature range from 0.26 to 1.30°K. The best fit for the SF-to-P critical field up to 0.70°K was found to be H_c (SF-to-P) $=H_{c0}(1-CT^n)$, where $H_{c0}=20.6\pm0.03$ kOe, $n=1.82\pm0.10$, and $C=0.228\pm0.002$.

Single crystals of $MnCl_2 \cdot 4H_2O$ were grown by evaporation from saturated solutions at room temperature. $MnCl_2 \cdot 4H_2O$ has a monoclinic structure[1] with the angle $\beta=99°6'$. The crystals grow with the bc' plane prominent. The orientations of the crystal axes were determined by x-ray precession techniques. Most of the measurements were made with the external field parallel to the c' axis ($\perp$ to ab plane), and it is believed that this is the most preferred direction for this crystal.

The external field was produced by a superconducting solenoid. The differential susceptibility $\chi=dM/dH$ was determined by measuring the mutual inductance of a pair of coils surrounding the sample. A Cryotronics mutual inductance bridge was employed for these measurements. The coils were similar to those described by various authors[2,3] for magnetic temperature measurements at very low temperatures.

A He^3 refrigerator was used to obtain temperatures below 1.2°K. The temperature was determined by

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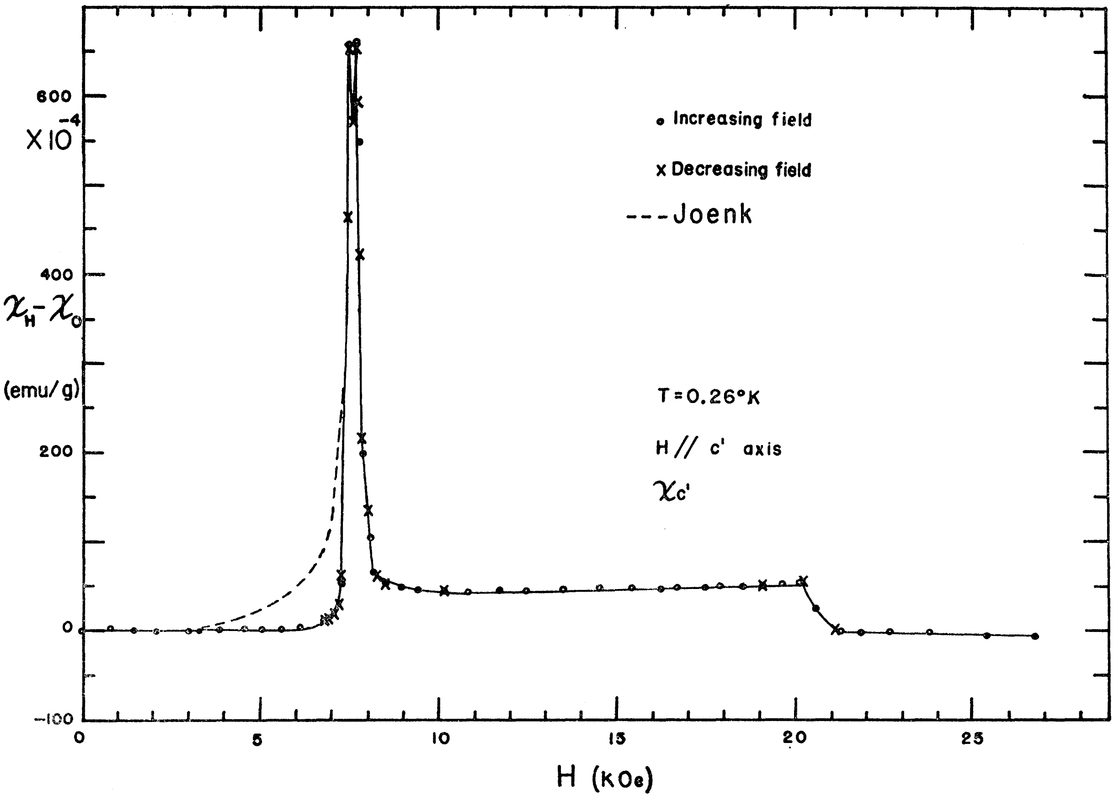

FIG. 1. ac susceptibility in emu/g of $MnCl_2 \cdot 4H_2O$ at 0.26°K. Solid line is drawn through experimental points. The small dots are data taken with field increasing and crosses are data taken with field decreasing. Dashed line is calculated from work of Ref. 8.

measuring the vapor pressure of liquid He^3 contained in a separate bulb in thermal equilibrium with the refrigerator. Pressure measurements were made with a Texas Instruments fused quartz pressure gauge.

The sample was composed of two single crystals of $MnCl_2 \cdot 4H_2O$ with a combined mass of 1.783 G. The crystals were orientated such that the external field and the measuring field (~0.5 Oe) were parallel to the desired crystalline axis. The crystals were always in thermal equilibrium with the He^3 refrigerator.

Previous experimental evidence for the existence of the spin-flop phase in $MnCl_2 \cdot 4H_2O$ has, with one exception, been limited to the temperature region above 1°K. Gijsman *et al.*[4] observed that the magnetization

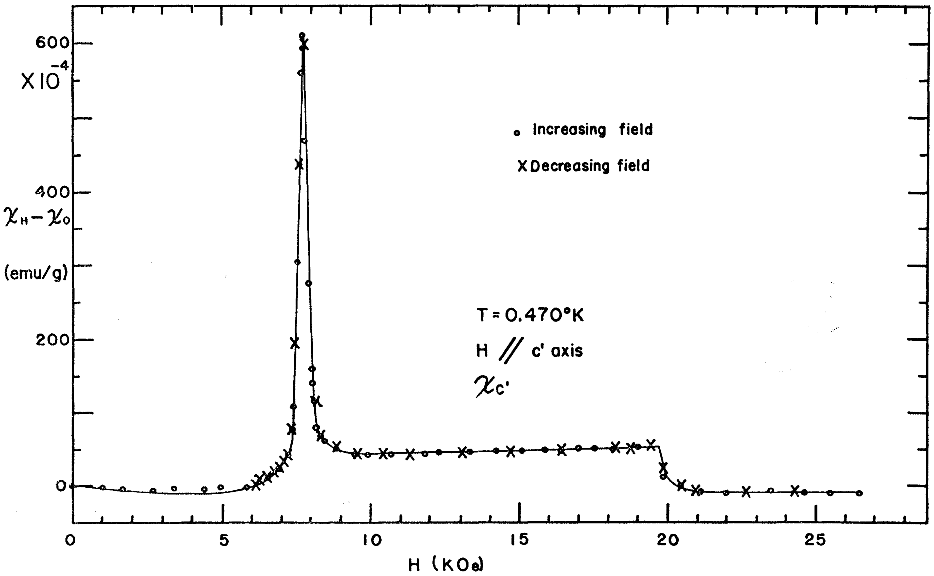

FIG. 2. ac susceptibility in emu/g of $MnCl_2 \cdot 4H_2O$ at 0.470°K.

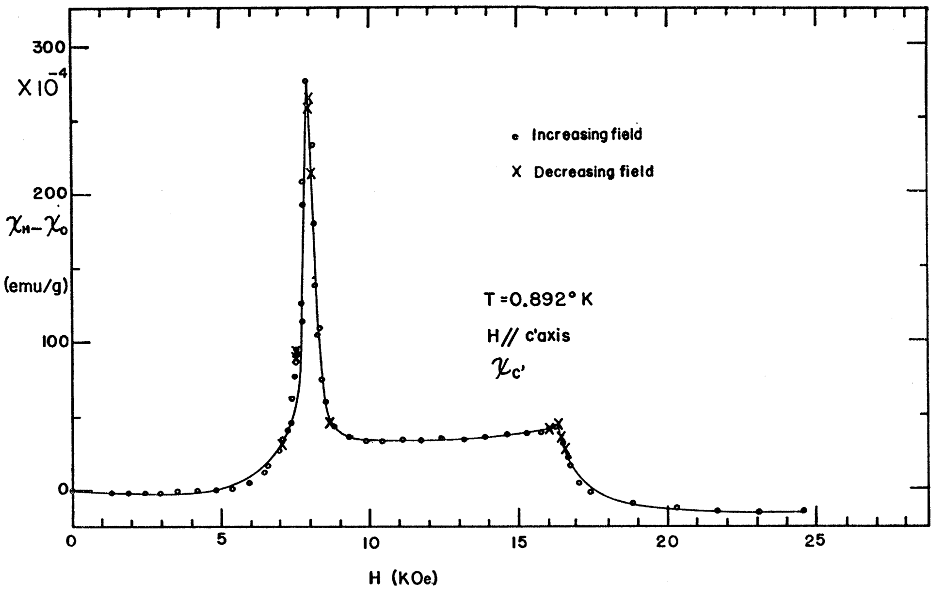

FIG. 3. ac susceptibility in emu/g of $MnCl_2 \cdot 4H_2O$ at 0.892°K.

increased rapidly with field in the neighborhood of 7500 Oe along the *c*′ axis at 1.02°K. They also observed a zero-frequency electron resonance between 1.02 and 1.21°K at slightly higher fields which was interpreted as the spin-flop threshold field. Tsujikawa and Kanda[5] observed the absorption spectrum of $MnCl_2 \cdot 4H_2O$ down to 1.2°K and attributed an anomalous behavior between 5.0 and 10 kOe to spin flop. Friedberg and Schelleng[6] adiabatically magnetized $MnBr_2 \cdot 4H_2O$ at 1.5°K and observed an energy release at about 9 kOe which was probably due to spin flop, but were unable to obtain reproducible results upon demagnetizing below 9 kOe.

The only known work which extends well below 1°K

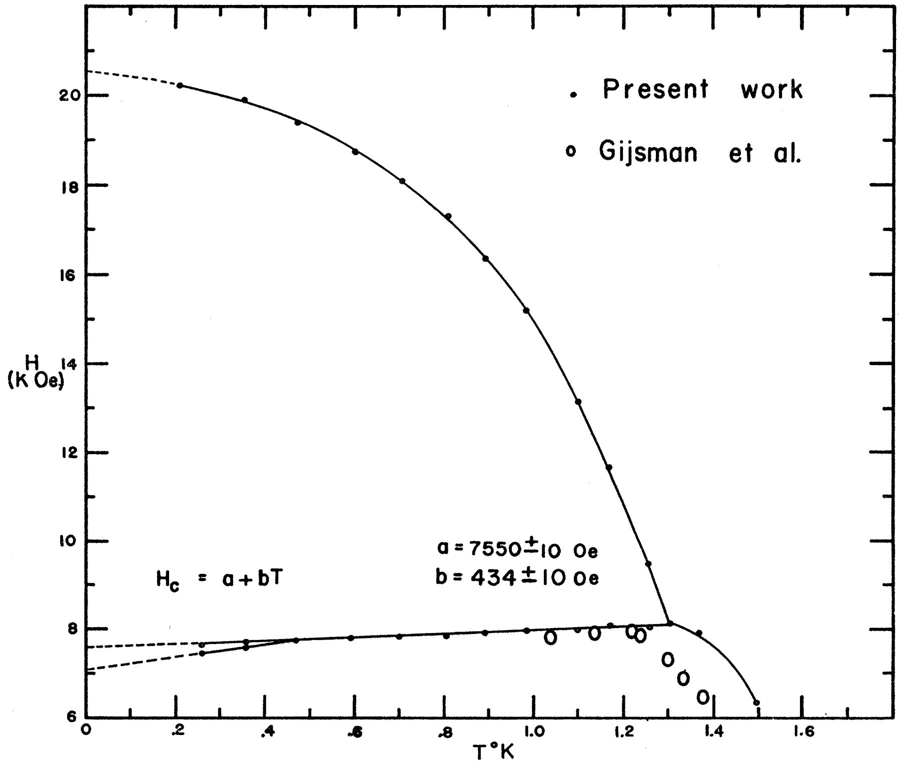

FIG. 4. *H*-*T* Phase Diagram of $MnCl_2 \cdot 4H_2O$. Solid lines are drawn through experimental points. Dashed lines are extrapolations of experimental data to $T = 0°K$. Open circles are from the zero-frequency electron-resonance data of Ref. 4.

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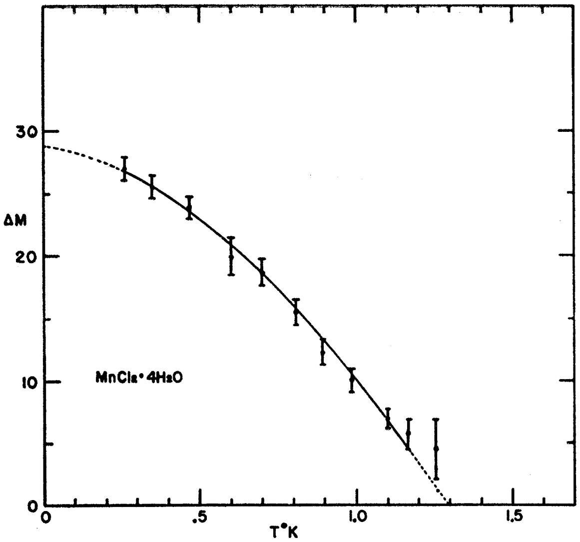

FIG. 5. Change in magnetization across the antiferromagnetic–to–spin-flop phase boundary in Oe/g.

on $MnCl_2 \cdot 4H_2O$ is the antiferromagnetic resonance data of Abkowitz and Honig[7] between 0.32 and 1.62°K.

The results of our calculations of χ_c, at 0.26°K are shown in Fig. 1, where we have plotted $\chi(H)-\chi(0)$ against H. The large narrow peak at about 7.5 kOe clearly distinguishes the AF-to-SF transition. In the spin-flop state the magnitude of χ reflects the fact that one is now measuring $\chi_\perp$. The value of χ between 8.5 and 20.0 kOe in these measurements agrees quite well with the low-field value of χ_b which was determined in a different run. At 20.20 kOe the slope of $\chi_{c'}$ changes abruptly. Above this field $\chi_{c'}$ drops rapidly and approaches zero as saturation is approached. The field at which the abrupt change in slope takes place is interpreted as the critical field for the SF-to-P transition.

Joenk[8] extended the spin-wave theory to predict the behavior of $\chi\,||$ as a function of external field and temperature in the antiferromagnetic phase. His results should be valid up to within 1% of the AF-to-SF critical field. By normalizing to the experimental results at $0.99H_c$, a comparison of the present data to his predictions is made. The values of χ calculated in this way are shown as a dashed line in Fig. 1. It can be seen that the experimental peak is much sharper than the predicted behavior.

The data at 0.47 and 0.892°K are shown in Figs. 2 and 3. In all, measurements were made at eleven different temperatures from 0.26 and 1.30°K. The phase diagram obtained from these data is plotted in Fig. 4.

At all temperatures below 0.5°K two distinct peaks were observed. Repeated passes through the region of these peaks confirmed their existence. In a later measurement one of the two crystals was removed, and only a single peak was produced. The small difference in critical field for the two crystals (about 100 Oe) at the lowest temperature could have been due to a slight misalignment of the crystals or a difference in internal field caused by strains. The lower field peaks are also plotted in Fig. 4, where it can be seen that the two merge in the neighborhood of 0.5°K. Some of the zero-frequency electron-resonance data of Gijsman *et al.*[4] are plotted as large circles for comparison.

In one set of runs the external field was placed along the b axis of the crystal and χ_b measured as a function of field at 0.4°K. At low fields the susceptibility is roughly constant with a magnitude $\chi_b=4.5\times10^{-3}$ emu/g. This is within a few percent of the magnitude of $\chi_{c'}$ in the spin-flop region.

However, at 8.5 kOe, a transition, similar to the SF-to-P transition, takes place. χ_b decreases more slowly toward saturation than $\chi_{c'}$, but in both cases saturation takes place somewhat above 20 kOe.

Gorter and Peski-Tinbergen[9] have used the original Néel molecular-field theory for the particular case of orthorhombic symmetry, and $S=\frac{1}{2}$ to predict the behavior of antiferromagnetic materials in external fields. Gijsman *et al.*[4] extended this work to arbitrary spin value and applied it to monoclinic $MnCl_2 \cdot 4H_2O$.

If the external field is along the most preferred direction (x direction), one obtains the following limiting values for the phase-transition boundaries:

$$kT_N=(S+1)(A_x+D_x)/3S, \qquad \text{for } H=0 \tag{1}$$

$$\mu H_{c1}=[(A_x+A_y-D_x+D_y)(A_x-A_y+D_x-D_y)]^{1/2}, \qquad \text{for } T=0 \tag{2}$$

$$\mu H_{c2}=A_x+A_y-D_x+D_y, \qquad \text{for } T=0. \tag{3}$$

In the above equations, A_x and A_y are the coefficients of antiferromagnetic interaction between the sublattices and D_x and D_y are the coefficients of ferromagnetic (>0) or antiferromagnetic (<0) interaction inside one sublattice. We let H_c (AF-to-SF) $=H_{c1}$ and H_c (SF-to-P) $=H_{c2}$. It is assumed that $\mu_x=\mu_y=\mu_z=\mu=2\beta S$, and the x, y, z axes are the most preferred, next preferred, and least preferred directions, respectively.

TABLE I. Increase in magnetization per gram, and the latent heat per mole for the antiferromagnetic–to–spin-flop transition in $MnCl_2 \cdot 4H_2O$.

Temp (°K)	ΔM (per g)	l (J/mole)
0.26	27.0	0.0343
0.348	25.6	0.0436
0.470	23.9	0.0549
0.600	19.9	0.0582
0.700	18.7	0.0640
0.807	15.5	0.0611
0.892	12.2	0.0532
0.983	10.1	0.0487
1.098	7.1	0.0378
1.167	5.8	0.0332
1.256	4.6	0.0282

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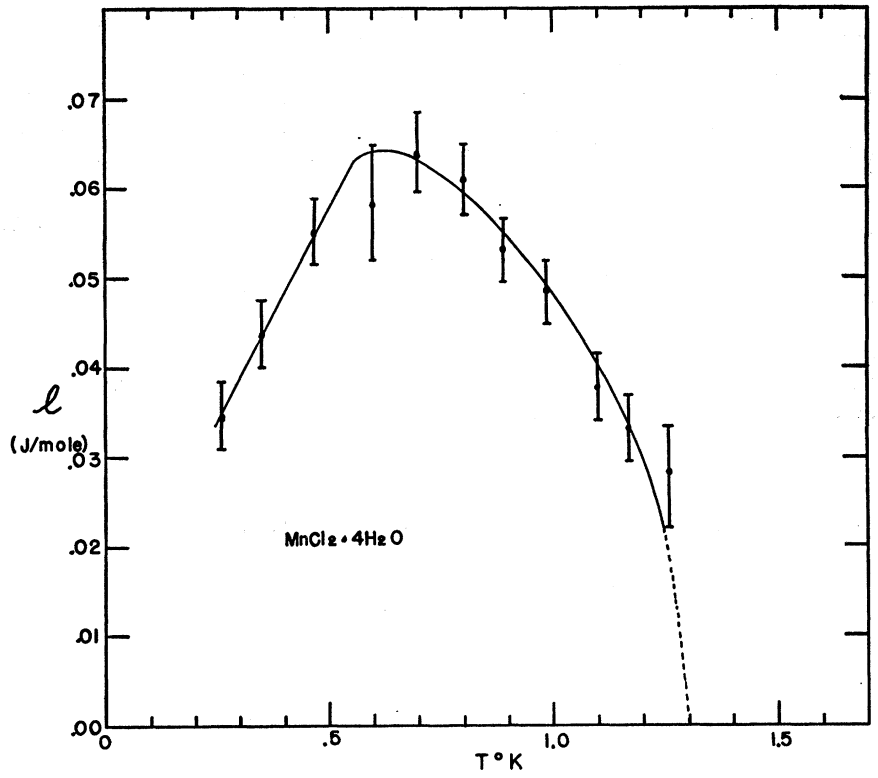

FIG. 6. Latent heat of transition in J per mole for the antiferromagnetic-to-spin-flop transition.

If the external field is along the y direction, one obtains one transition to a parallel aligned state along the y direction at a field:

$$\mu H_y = A_x + A_y + D_x - D_y, \qquad \text{for } T=0. \qquad (4)$$

The present data give $H_{c1}=7.55\times10^3$ Oe, $H_{c2}=20.6\times10^3$ Oe, and $H_y=8.5\times10^3$ Oe. The value of T_N is taken as 1.62°K.

Using Eqs. (2)–(4), one obtains $A_x=4.24k$, $A_y=1.04k$, $D_x-D_y=-2.19k$. If Eq. (1) is used with Eq. (5) to obtain D_x one gets $D_x=-0.776k$, $D_y=1.42k$. These values are in extreme disagreement with those of Gijsman *et al.*,[4] obtained from their susceptibility data. The most important difference is in the sign of D_y, where our results indicate a rather large ferromagnetic interaction within the sublattice instead of an antiferromagnetic interaction. This discrepancy would indicate that the theory is not applicable to $MnCl_2 \cdot 4H_2O$ It does, however, predict the correct qualitative behavior of the system.

Considerable attention has been given to the exact nature of the AF-to-SF transition. Gorter and Peski-Tinbergen,[9] and Anderson and Callen,[10] in particular, point out that if the transition is of first order then there will probably be a considerable hysteresis. In fact, Anderson and Callen predict a difference of about 12% in the values of $H_c(1)$ obtained by going through the transition in opposite directions.

Experimentally, no hysteresis was observed. Figure 1 shows the results at 0.26°K for several passes through the transition in both directions. The reproducibility of the data was as good as the ability to reset the exact field (~10 G). However, the transition does not take place instantaneously. If the field were changed, by say 100 Oe, in the immediate vicinity of the peak, equilibrium for the new field setting would take from 5–10 min. All points were taken only after the system had been in equilibrium for several minutes.

If on the other hand a rapid pass were made through the transition, an apparent hysteresis would be observed. This was clearly demonstrated in one early run at 0.4°K. After both transitions had been observed by monotonically increasing the field in steps to 27 kOe, the field was reduced to zero continuously over a period of about 25 min. When the peak failed to show up on subsequent magnetizations, the cryostat was opened and the crystal was found to have rotated 90° in its holder so that the b axis was aligned along the external field. In this case, the field was reduced considerably below the critical value before the spin system could relax from the spin-flop orientation back to the antiferromagnetic orientation. The resulting torque rotated the crystal.

Assuming, as predicted, that the AF-to-SF transition is of first order, the change in magnetization which occurs in going from the AF state to the SF state was calculated by measuring the area under the susceptibility peaks. The results are shown in Fig. 5. The latent heat of transition was then calculated using the Clapeyron equation. The results are plotted in Fig. 6,

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and together with the change in magnetization are tabulated in Table I. The error in these numbers is estimated to be less than 10% at the lowest temperatures, increasing to about 30% above 1.0°K. The values of ΔM and l at 1.256° K are probably too large. It was difficult in this case to judge how much area to include in the ΔM calculation due to the broadness of the peak and the small separation between the two transitions. If ΔM and l are extrapolated to zero at 1.30°K, then the quoted values of these quantities at 1.256°K fall well above the smooth curve.

It might be well to point out, in conclusion, that according to Anderson and Callen[10] the temperature dependence of the SF-to-P transition boundary should determine how spin-wave renormalization should be carried out. That is, if spin-wave energies are renormalized by the energy then the temperature dependence should be $T^{5/2}$; however a $T^{3/2}$ dependence is expected if the energy is renormalized by the magnetization. Our results show that the actual dependence is $T^{1.82}$ which would indicate that the $T^{3/2}$ term is dominant.

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PHYSICAL REVIEW VOLUME 162, NUMBER 2 10 OCTOBER 1967

Spin-Echo and Free-Induction-Decay Measurements in Pure Fe and Fe-Rich Ferromagnetic Alloys: Domain-Wall Dynamics

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Measurements were made of the free-induction-decay (FID) and spin-echo amplitudes of Fe^{57} in pure Fe and some of its alloys. Complex spectra are observed consisting of many oscillations often covering a range of many Mc/sec. The amplitudes are very dependent on the pulse length τ, the applied rf field B_1, and the exciting frequency ω. Excellent agreement is found between the experimental and calculated amplitudes when a model for domain-wall motion is used which takes into consideration the following features: 1. There is an averaging over the orientation of $\mathbf{B}_1$ with respect to the local magnetization. 2. There is a variation of the enhancement factor across the domain wall due to the spin arrangement in the wall. 3. The domain wall is considered to be composed of area segments which are immobile along their perimeters and whose motion resembles that of a vibrating drumhead. 4. These domain-wall segments have a distribution in areas. The restricted motion of the domain walls imposed by the last two features is essential in order to obtain agreement with the experimental results. This is in contrast to the usual model, which represents the domain-wall motion as given by rigid simple-harmonic-like oscillations; such a model shows great discrepancy with the experimental results presented here. In some of the spectra, asymmetries are observed in the variation of the amplitudes as a function of frequency. No satisfactory explanation for these asymmetries is known although some possible sources are suggested. Such asymmetries make it appear very doubtful that the Fe-alloy spectra obtained with this technique can be reliably unfolded to give the variation of the internal field for second- or higher-neighbor impurity atoms. FID amplitude measurements were also made on Fe in an externally applied dc field. No variation in the value of the maximum enhancement factor was observed for dc fields varying from 0 to about 5 kG.

I. INTRODUCTION

Several investigators[1–3] have been using spin-echo techniques to try to measure the variation of the internal field at different occupational configurations in ferromagnetic alloys. The hope is then to correlate the measured internal fields with the various neighbor shells of solute atoms and thus obtain the spin-density variation as a function of distance from the magnetic ion. When measurements were made on the same Fe alloys with both NMR (Nuclear Magnetic Resonance) and Mössbauer techniques,[3,4] it was found that the two methods did not give the same shifts for second- and third-nearest neighbors and, moreover, that the shape of the spectra obtained with NMR did not vary in a manner consistent with the calculated abundance of the various occupa-

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