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Antiferromagnetic Resonance*

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The frequencies at which electronic resonance will occur apparently lie beyond the region now available with conventional microwave equipment for those materials having Curie temperatures well above 0°K. Cr_2O_3, MnO, MnTe, and MnSe show a large decrease in the amount of resonance absorption as the material (powdered) is lowered through its Curie temperature, with only a small residual absorption remaining in the antiferromagnetic region. MnSe has an absorption *vs* temperature hysteresis loop that is correlated with a magnetic susceptibility loop previously reported for this material. The *g* values remain constant as the absorption decreases. Considerable absorption is found at zero static magnetic field for MnO, MnS, and MnTe. The line widths increase sharply as the temperature of the material approaches the Curie temperature. CoO and VO_2 give no detectable absorption either above or below their Curie temperatures. NiO and CuO show no absorption in the antiferromagnetic region.

I. INTRODUCTION

The problem of predicting electronic resonance in the antiferromagnetic state is essentially a problem of understanding the behavior of the normal frequencies of precession of two sublattices of magnetization having oppositely directed spins. Once the normal frequencies are determined, then one can expect with certainty that magnetic resonance absorption will occur when the frequency of the applied transverse rf field is equal to a normal frequency. Although in actual experiments there may exist more than one sublattice in one direction, the experiment deals, in effect, with only two groups of spins; within each group each spin feels the same anisotropy and exchange fields.

The initial investigation[1] studied experimentally the change in absorption at 9300 Mc in going from the paramagnetic to the antiferromagnetic region for Cr_2O_3 by our group at the Naval Ordnance Laboratory. Similar work[2] was carried out on MnF_2 by Hutchison at the University of Chicago. These investigations showed a sharp break in the absorption as the material was cooled through its Curie temperature (T_c) with either no measurable absorption or only a small residual existing below T_c. As a result of this work, we believed that the normal frequencies of these materials lay beyond the region obtainable by our equipment. However, Okamura, Torizuka, and Kojima[3] reported appreciable amounts of absorption for MnO, MnS, and MnSe below the Curie temperature, with no sudden drop as had been found for Cr_2O_3 and MnF_2. The reason for this difference in response of these materials was not apparent.

Kittel[4] and Nagamiya[5] have calculated the equations of motion of the antiferromagnetic system where the exchange forces are treated as molecular fields and where, similar to the ferromagnetic case, an anisotropy term is introduced to take into account the turning of both spin systems together and relative to a cubic crystal lattice at 0°K. From this one obtains the resonance frequency as

$$\omega_0/\gamma = H_0 \pm [H_a(H_a+2H_e)]^{\frac{1}{2}}, \tag{1}$$

where H_0 is the static applied magnetic field, H_a and H_e internal fields describing the anisotropy and exchange fields. Physically this means that there should exist two different directions of circular polarization both of which are capable of being excited by the rf field. For the materials mentioned above, which have relatively high Curie temperatures, H_e is of the order of 10^6 oersteds and much larger than either H_0 or H_a, in which case Eq. (1) reduces to a single frequency

$$\omega_0/\gamma = (2H_aH_e).^{\frac{1}{2}}, \tag{2}$$

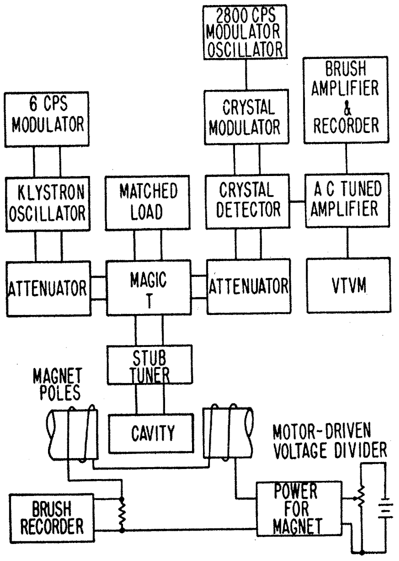

FIG. 1. Block diagram of microwave apparatus for recording magnetic resonance absorption.

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[*] Supported in part by the U. S. Office of Naval Research.

[1] Trounson, Bleil, Wangsness, and Maxwell, Phys. Rev. **79**, 542 (1950); L. R. Maxwell, Am. J. Phys. **20**, 80 (1952).

[2] Reported by private communication (see also second paper reference 1).

[3] Okamura, Torizuka, and Kojima, Phys. Rev. **82**, 285 (1951).

[4] C. Kittel, Phys. Rev. **82**, 565 (1951).

[5] T. Nagamiya, Prog. Theoret. Phys. **6**, 350 (1951).

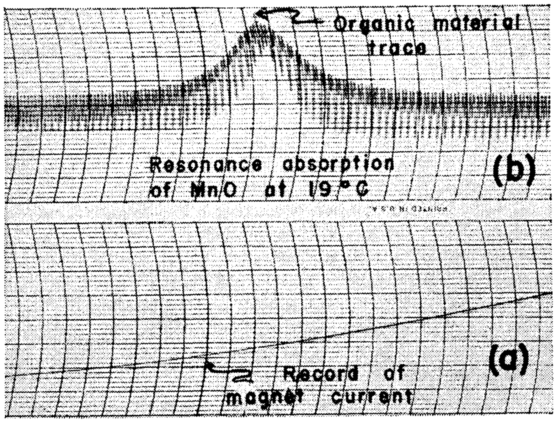

FIG. 2. Photograph of a recorded record showing a resonance curve for MnO.

From Eq. (2) we estimate that for no external static magnetic field the resonance frequency is beyond the range available with conventional microwave equipment. For MnF_2 Keffer[6] predicts resonance at a wavelength of 1.1 mm at 0°K.

The classical calculations have been extended by Keffer and Kittel[7] to cover ellipsoidal shapes, orthorhombic symmetry, and a generalized two lattice anisotropy; they also included a quantum-mechanical derivation of the resonance equations which agreed essentially with the classical treatment. Wangsness[8] has shown that both antiferromagnetic and ferromagnetic resonance conditions are special cases of a more general system of two interpenetrating magnetic sublattices.

The theory calls for the appearance of a doublet as the material is cooled through the Curie temperature, once the frequency and static magnetic field are within proper values. The existence of two electronic resonance absorption bands have been reported by Poulis *et al.*[9] at 9400-Mc region for $CuCl_2 \cdot 2H_2O$ at low temperatures where the exchange forces are weak. Ubbink[10] has interpreted their results on the basis of antiferromagnetism at absolute zero in a crystal having rhombic symmetry.

We wish now to confine our attention to experimental investigations of antiferromagnetic materials having Curie temperatures above liquid nitrogen temperature, using 3-cm equipment, and to study the change in the nature of the absorption as one approaches and passes through the Curie temperature. We shall report on recent work carried out at the Naval Ordnance Laboratory on various powdered materials, including the manganese compounds studied by the Japanese.

II. EXPERIMENTAL PROCEDURE

A. Experimental Method

We use the procedures developed by other investigators for paramagnetic resonance. The sample is located at the bottom of an iris coupled resonant cavity, placed in the presence of an external steady magnetic field in a direction perpendicular to the rf magnetic field. The absorption is detected as a change in intensity of reflection from the cavity. At resonance we have[11]

$$\frac{P_r}{P_i}=\left[\frac{(Q_e/Q_0)-1}{(Q_e/Q_0)+1}\right]^2, \tag{3}$$

where P_i = power incident upon the cavity; P_r = power reflected from the cavity; Q_e (external Q) = $\pi\times$energy stored in cavity/energy lost per $\frac{1}{2}$ cycle external to the cavity; Q_0 (unloaded Q) = $\pi\times$energy stored in cavity/energy lost per $\frac{1}{2}$ cycle in the cavity. We define Γ by

$$|\Gamma|=(P_r/P_i)^{\frac{1}{2}},$$

express

$$1/Q_0=(1/Q_w)+(1/Q_M),$$

and define Q_L by

$$1/Q_L=(1/Q_w)+(1/Q_e),$$

where $1/Q_w$ and $1/Q_M$ are proportional to the losses in the walls of the cavity and to magnetic absorption of the material within the cavity, respectively.

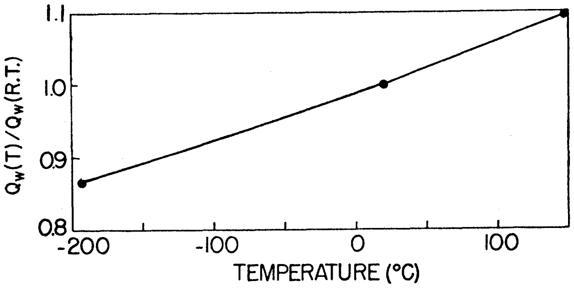

FIG. 3. Variation of $Q_w(T)/Q_w$(R.T.) with temperature.

Then one can formulate Eq. (3) as

$$\frac{Q_L}{Q_M}=\frac{|\Gamma|-|\Gamma_0|}{1-|\Gamma|}, \tag{4}$$

which is the expression given by Whitmer and Weidner,[12] where

$$|\Gamma_0|=(P_{r_0}/P_i)^{\frac{1}{2}} \tag{5}$$

is the reflection for $H=0$. Upon application of the magnetic field, P_r may decrease in a manner defined as

$$P_r=P_{r_0}(1-S). \tag{6}$$

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[6] F. Keffer (to be published).

[7] F. Keffer and C. Kittel, Phys. Rev. **85**, 329 (1952).

[8] R. K. Wangsness, Phys. Rev. **86**, 146 (1952).

[9] Poulis, van den Handel, Ubbink, Poulis, and Gorter, Phys. Rev. **82**, 552 (1951); J. Ubbink, Proc. Conf. Low Temp. Phys. Oxford (1951), p. 163.

[10] J. Ubbink, Phys. Rev. **86**, 567 (1952).

[11] R. D. Arnold and A. F. Kip, Phys. Rev. **75**, 1199 (1949).

[12] C. A. Whitmer and R. T. Weidner, Fifth Annual Progress Report on Nuclear and Electronic Paramagnetism and Low Temperature Studies (1951), p. 24; R. T. Weidner and C. A. Whitmer, Rev. Sci. Instr. **23**, 75 (1952).

Substituting Eqs. (5) and (6) in Eq. (4) we have, for $S^2<1$ neglecting terms of S^3 and higher powers,

$$\frac{Q_L}{Q_M}=\frac{\frac{1}{2}S+\frac{1}{8}S^2}{1-\frac{1}{2}S-\frac{1}{8}S^2-(Pi/Pr_0)^{\frac{1}{2}}}. \tag{7}$$

The magnetic loss is approximately linear with S provided that

$$(Pi/Pr_0)^{\frac{1}{2}}\geqq 3.$$

B. Experimental Arrangement

Figure 1 indicates, by means of a block diagram, the essential units required for measuring the electronic resonance. The microwave power is furnished by a klystron oscillator operating at a frequency of approximately 9300 Mc under the influence of a low frequency modulator arranged to vary the reflector voltage. By this method the energy incident upon the magic tee is frequency modulated about 6 times each second. The material under examination is placed in a rectangular cavity located between the pole pieces of an electromagnet with the static and alternating magnetic fields arranged orthogonally. Detection of the unbalance is made through the combination of a crystal modulator and detector; the latter is connected to an amplifier and recorded (I). The current through the windings of the electromagnet is recorded by a second brush recorder (II).

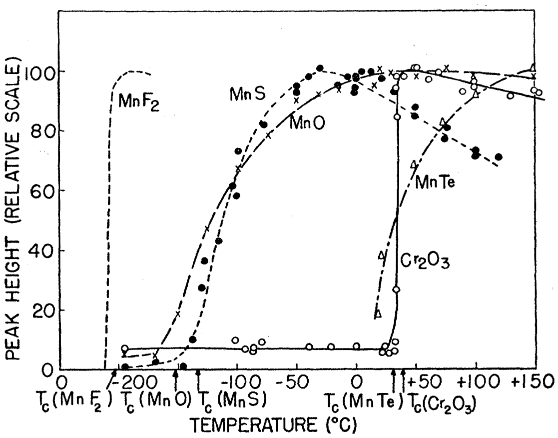

FIG. 4 Variation of the height of the resonance absorption with temperature.

Figure 2 illustrates a typical record made with the apparatus described above. A typical record of II is shown in Fig. 2(a) which gives an approximate linear variation in current with time. Power for this current is provided by an electronic power supply whose output is grid controlled through a motor driven voltage divider. The output from the detector is shown in Fig. (2b) as a trace oscillating at the frequency of the modulator. By varying the frequency of the klystron in this manner it is possible always to pass through the resonance frequency of the cavity. This procedure is somewhat similar to the method used by Whitmer and Weidner.[12] A specimen of diphenyl trinitrophenyl hydrazyl was usually added to the cavity to be used in determining the g values. This material produces a narrow pip superimposed upon the absorption record [see Fig. 2(b)].

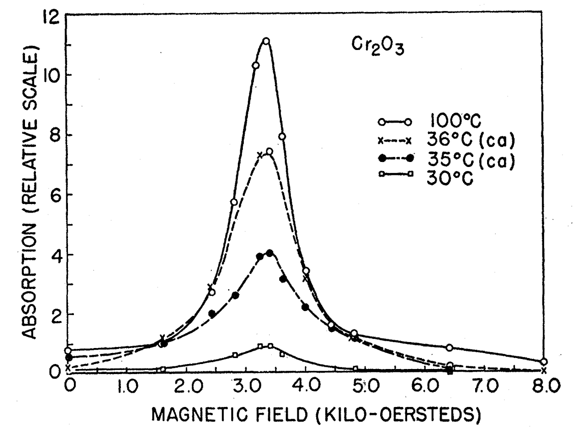

FIG. 5. Resonance curves for Cr_2O_3 taken at various temperatures.

The zero absorption has been arbitrarily defined as the amount of absorption existing at the maximum magnetic field used (approximately 8000 oersteds). The envelope formed by the upper portion of the trace shown in Fig. 2(b) gives the absorption of the material as a function of the applied static magnetic field and is a measure of the quantity S which is proportional to the magnetic absorption.

We have considered above that Q_w is temperature independent. Measurements made at various temperatures with the cavity empty gave a variation of $Q_w(T)/Q_w$ (room temperature) as illustrated by Fig. 3. These changes due to temperature variation were small compared to the changes in the magnetic losses which were found to occur in the neighborhood of the Curie temperatures and were therefore neglected.

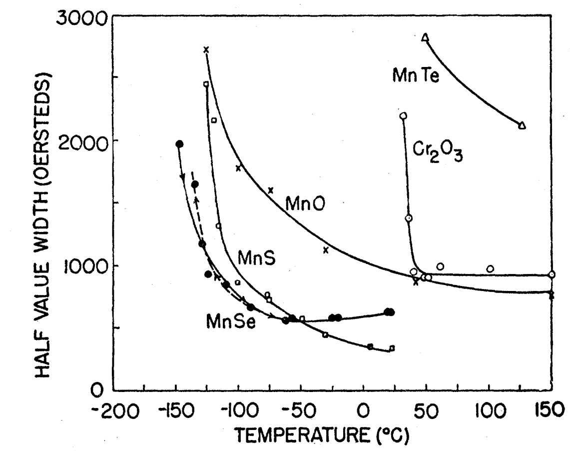

FIG. 6. Variation of half-value widths with temperature.

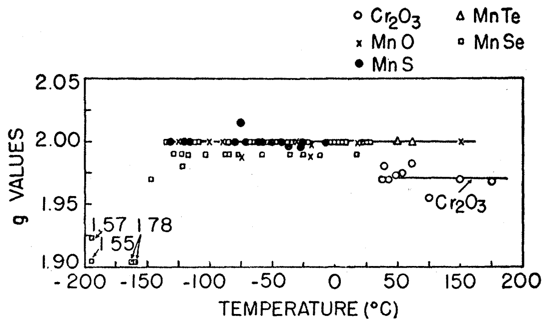

FIG. 7. Summary of *g* values.

III. RESULTS

Except for certain of the compounds given below, we have obtained as a function of the temperature the height of the peak absorption (normalized to 100 at the maximum), the absorption as a function of the applied static magnetic field, half-value widths, and *g* values. The *g* values have been determined with reference to the value of 2.004 reported[13] for diphenyl-trinitrophenyl hydrazyl. This value is temperature independent.[12] All data are for powdered material.

1. Cr_2O_3

Recent data have been obtained with a sample of high purity (Johnson, Matthey, and Company) which gives a variation of peak height *vs* temperature as shown in Fig. 4. This is essentially the same type of curve reported previously by us[1] but with a lesser slope above the Curie temperature. We find, for this material, that the temperature-dependent peak reported previously[1] is absent. As seen in Fig. 5 the absorption decreases to a small residual below the Curie temperature. The half-value width increases abruptly at the Curie temperature (Fig. 6). The *g* values, except for some scatter, are temperature independent at about 1.97, as seen in Fig. 7, and are significantly less than 2.00.

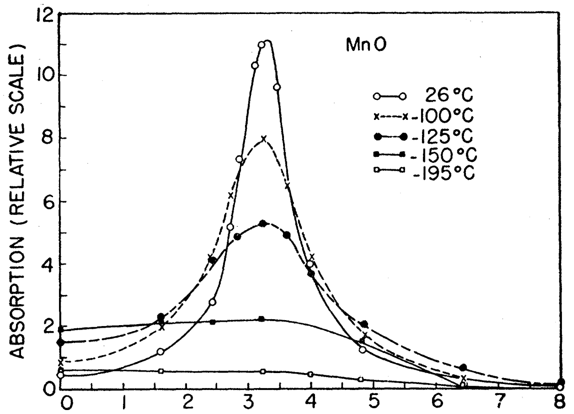

FIG. 8. Resonance curves for MnO taken at various temperatures.

2. MnO

As contrasted to Cr_2O_3, the peak absorption decreases more gradually as the Curie temperature is reached and then levels off to a small residual (Fig. 4). The absorption diminishes and broadens as the Curie temperature is reached, losing its resonance characteristic (as shown in Fig. 8). It shows considerable absorption at zero magnetic field at −150°C. This fact was not evident in the preliminary measurements[1] made on this material because of insufficient data at the higher magnetic fields where zero absorption is fixed. The *g* values are independent of temperature and close to 2.00 (Fig. 7).

3. MnS

The peak absorption goes through a maximum at about −50°, dropping to a small residual below its Curie temperature. Similar to MnO, we find a broad absorption near the Curie temperature (Fig. 9) with appreciable absorption at zero magnetic field at −133°C. The half-value widths increase rapidly near the Curie temperature as seen in Fig. 6. The *g* values are close to 2.00 (Fig. 7).

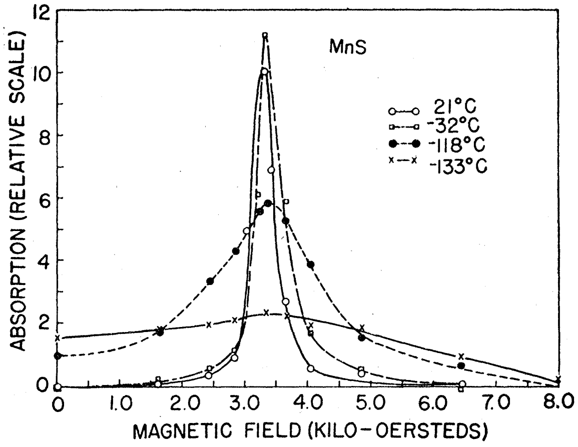

FIG. 9. Resonance curves for MnS taken at various temperatures.

4. MnTe

The magnetic absorption was considerably weaker for MnTe than for the materials mentioned above. This fact is not apparent from Fig. 4 because of the normalization. It was observed, however, that the peak absorption decreased to a small value below the Curie temperature. Again broad absorption was found below the Curie temperature (Fig. 10). Large half-value widths were found (Fig. 6) and *g* values are 2.00.

5. MnSe

Above the Curie temperature the peak absorption shows a temperature hysteresis loop as illustrated in Fig. 11. The loop opens at about room temperature and

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[13] Holden, Kittel, Merritt, and Yager, Phys. Rev. **77**, 147 (1950).

closes at approximately −150°C, and then the absorption drops to a small residual at liquid air temperature. The upper portion of the loop is formed during the cooling part of the cycle. Figure 12 gives the variation of absorption with external static magnetic field as the temperature of the material is decreasing. The absorption broadens as the temperature approaches −150°C, showing definite absorption at zero field at −134°C. The half-value width, for both decreasing and increasing temperature, are given in Fig. 6; a slight hysteresis loop is present. At temperatures from about −150°C to liquid nitrogen there was a small residual peak, not illustrated in Fig. 12, that moved off the resonance condition to give low g values as shown in Fig. 7. At −130°C and above, the g values were temperature independent and scattered between 2.00 and 1.99.

6. CoO

With a Curie temperature of 12°C it was possible to investigate CoO both in the paramagnetic and antiferromagnetic region. Throughout the region studied, from −195°C to 25°C, no measurable absorption was detectable.

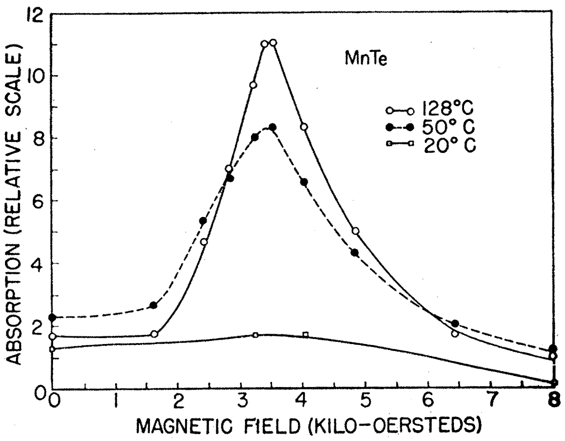

FIG. 10. Resonance curves for MnTe taken at various temperatures.

7. NiO

Only measurements below the Curie temperature (378°C) were made which gave no absorption.

8. CuO

No magnetic absorption was detectable in the antiferromagnetic region. The Curie temperature was approximately 250°C.

9. VO_2

Over the temperature region 25°C to 100°C no magnetic absorption was observed. The Curie temperature of VO_2 is about 60°C.

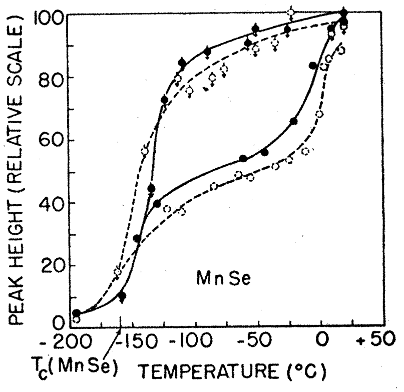

FIG. 11. Variation of peak height with temperature for MnSe for two sets of data.

IV. DISCUSSION

For all of these materials that exhibit paramagnetic resonance, we find that as the temperature is lowered through the Curie temperature, the amount of absorption decreases, the peaks broaden, and at a few degrees below the Curie temperature the absorption either disappears or remains as a low residual. In many instances, there is an appreciable amount of absorption at zero magnetic field. The abruptness of the decrease in absorption is greater for Cr_2O_3 and MnF_2 than for MnS, MnSe, MnTe, and MnO; the latter shows the slowest decent. This is illustrated in Fig. 13, where both temperature and peak heights are normalized.

Our data do not agree with the work reported by Okamura *et al.*[3] for MnO, MnS, and MnSe except in certain general features. We have no explanation for this difference. Our results not only conform to what one would expect from the theory, but, together with the response shown by Cr_2O_3 and MnF_2, they give a consistent picture of this phenomena at the temperatures investigated.

The hysteresis loop found for MnSe (Fig. 11) follows approximately a similar loop reported by Lindsay[14] for the variation of the magnetic susceptibility with temperature. He suggested that there exists three

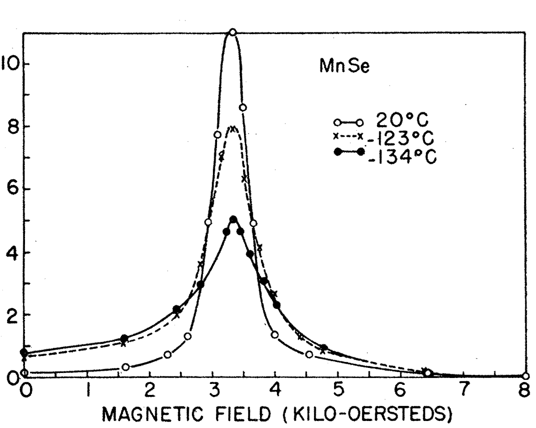

FIG. 12. Resonance curves for MnSe taken during decreasing temperature cycle.

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[14] R. Lindsay, Phys. Rev. 84, 569 (1951).

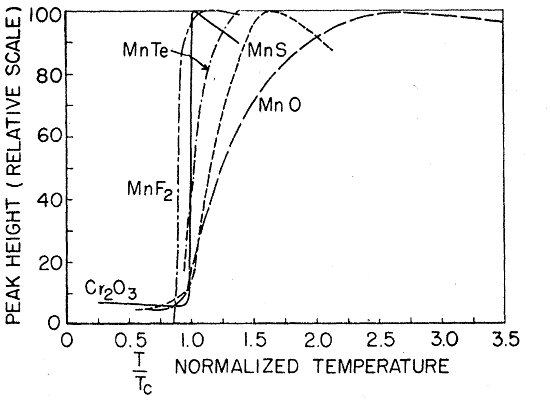

FIG. 13. Variation of the height of the resonance absorption with temperature normalized to the Curie temperature.

separate phases of MnSe. The presence of the loop is taken as a measure of the amount of the various phases present, which depends upon whether the material has been heated or cooled prior to the time of the measurement.

Within the paramagnetic region one finds for Cr_2O_3, MnS, and to a lesser degree for MnO, an increase in absorption with decreasing temperature similar to the magnetic susceptibility relationship. The departure from this similarity occurs as the antiferromagnetic alignment sets in. If, in the antiferromagnetic state, the frequency of the field could be tuned to the normal frequencies of the magnetic lattice, one might find new correlations between resonance absorption and magnetic susceptibility.

The origin of the low residual absorption found for certain materials below the Curie temperature cannot be definitely determined. They may be due to traces of ferromagnetic impurities. In the case of Cr_2O_3, magnetic susceptibility measurements showed the presence of a ferromagnetic impurity, although spectroscopic measurements showed no trace of Fe, Co, or Ni.

Line broadening with reduction in absorption as the Curie temperature is reached is characteristic of all of the materials for which paramagnetic resonance absorption was found. This is the trend indicated by Tsuya and Ichikawa,[15] who have calculated the line width as a function of temperature but without including crystal anisotropy.

V. CONCLUSION

The experiments made at liquid nitrogen and higher temperatures, where the exchange forces are strong, show no appreciable resonance absorption in the antiferromagnetic state. The theory has been concerned with determining the frequency requirement for resonance and has indicated the experimental condition necessary to obtain resonance. These conditions can be met by studying materials that have low Curie temperatures, going to considerably higher frequency (millimeters or less), and by using intense external static magnetic fields. At the present time, with the exception of the work carried out in Leiden, the theory and experiment have not reached common ground in this respect.

The problems of line widths, relaxation times, and a calculation of the quantitative yield for resonance absorption remain as fruitful fields for further investigations.

VI. ACKNOWLEDGMENTS

We wish to thank Dr. R. K. Wangsness and Mr. E. P. Trounson for their interest and helpful suggestions, and Mr. E. Wenzel for his assistance in the experimental work carried out at the Naval Ordnance Laboratory.

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[15] N. Tsuya and Y. Ichikawa, Phys. Rev. 83, 1065 (1951); Sc. Reports, Tohoku University 35, 74 (1951).

DISCUSSION

A. I. SNOW, *Sinclair Research Laboratories, Inc., Harvey, Illinois:* In connection with Dr. Gorter's comments about the effects of differences in crystal structure on comparison of the Leiden work and the work of Maxwell and McGuire, it is interesting to note that the peak height and half-width curves for MnO, MnS, and MnTe obtained by Maxwell and McGuire show no abnormal changes although the crystal structures change from face-centered cubic (NaCl type) to hexagonal (probably NiAs type) as one goes from MnO to MnTe.