$T_N/(g-1)^2J(J+1)$ with the $c/a$ ratio in the rare-earth elements that possess antiferromagnetic behavior.

Table IV presents the value of $T_N/(g-1)^2J(J+1)$ versus $c/a$ ratio for the rare-earth elements Tb through Tm. These results are also presented in Fig. 12 versus $c/a$ ratio. It is seen from Fig. 11 that if the $c/a$ ratio in terbium is increased, the function $T_N/(g-1)^2J(J+1)$ decreases. McWhan et al. reported that the $c/a$ ratio in terbium increases approximately 2.3% at a pressure of about 60 kbars. Jamieson[15] also reports that the volume and the lattice constants of some rare-earth elements vary linearly with pressure to about 100 kbar. Therefore, in view of the lack of detailed data, we shall assume at present that the $c/a$ ratio in terbium also varies linearly with pressure. The increase in $c/a$ in terbium at a pressure $P$ kbar is thus estimated at $(P/60)$ 2.3%. This expression is used to determine the $c/a$ ratio in terbium at the various pressures employed in the present experiment. The results are included in Table V. The values of $T_N/(g-1)^2J(J+1)$ in terbium at the various pressures, that is as a function of $c/a$ ratio, are also included in Fig. 11. The results are seen to be in excellent agreement with the variation of $T_N/(g-1)^2J(J+1)$ with $c/a$ for the elements Tm through Tb. Therefore, it is not unreasonable at this

time to assume that the variation of the Rudermann–Kittel interaction or $T_N/(g-1)^2J(J+1)$ in the rare earths with pressure is due to the variation of the number of states and the density of states per energy level in the B.Z. with pressure, which is directly related to the variation of the $c/a$ ratio with pressure.

## CONCLUSIONS

1. The antiferromagnetic region in terbium appears to be present to at least 14.22 kbar.

2. The present results indicate that Robinson et al. and McWhan et al. measured the pressure-coefficient of the Néel temperature and not the Curie temperature.

3. The present results on the pressure-coefficient of the Néel temperature are in good agreement, within the accuracy of the experimental technique, with the results obtained using the transformer method.

4. As with the Néel temperature, the Curie temperature decreases with increasing pressure.

5. The function $T_N/(g-1)^2J(J+1)$ is a function of the $c/a$ ratio.

6. The effect of the pressure upon the Rudermann–Kittel interaction or upon $T_N/(g-1)^2J(J+1)$ appears to be largely due to the effect of pressure upon the number of states and the density of states per energy level in the B.Z. which is directly related to the effect of pressure upon the $c/a$ ratio.

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# Susceptibility-Derived Sublattice Magnetization in Antiferromagnets*

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A technique for deriving the sublattice magnetization in antiferromagnets from parallel-magnetic-susceptibility measurements is proposed. The relation between these quantities is derived by means of a molecular-field formalism. However, it is pointed out that the results should have a greater range of validity than the molecular-field theory itself. The theory is applied to the antiferromagnets $MnF_2$, $CuCl_2 \cdot 2H_2O$, and $FeF_2$ and the results are compared to those available for these materials from nuclear-magnetic-resonance and Mössbauer-effect measurements as well as the usual molecular-field results. It is found that the susceptibility-derived results are in excellent agreement with those obtained by direct measurements. A reduction of an order of magnitude in the error between calculated and observed magnetization curves is obtained by using the susceptibility-derived results instead of the usual molecular-field results.

## INTRODUCTION

IN order to calculate such statistical quantities as anisotropy, magnetostriction, magnetoelectric susceptibility, etc., in antiferromagnets, it is generally necessary to know the sublattice magnetization as a function of temperature. While by means of such

techniques as the Mössbauer effect, nuclear magnetic resonance (NMR), and neutron diffraction, a direct measurement of the sublattice magnetization may be made, the first two methods are useful only for special types of materials, while the latter, aside from requiring special equipment not commonly available, does not have high precision.

We here present a method for deriving the sublattice magnetization of a two-sublattice antiferromagnet from the experimental results for $\chi_{||}$, the susceptibility parallel to the material's antiferromagnetic axis. In doing this, we make use of the suggestion of Callen and

Shtrikman[1] that the functional relationship between the moments $\langle (S_j{}^z)^n \rangle$ of the spin operator for ion $j$ which follows from molecular-field theory has a greater range of validity than molecular-field theory itself. Thus we may derive the relation between the sublattice magnetization $M$ and $\chi_{||}$ using molecular-field theory without being unduly restricted by its inherent limitations.

As a check on the suggested method, we apply the above technique to the antiferromagnets $MnF_2$, $CuCl_2 \cdot 2H_2O$, and $FeF_2$. For $MnF_2$[2-6] and $CuCl_2 \cdot 2H_2O$,[6-8] the sublattice magnetization has been measured directly by NMR, while in the case of $FeF_2$,[6,9] the sublattice magnetization has been measured directly by a combination of NMR and Mössbauer techniques. We find that the susceptibility-derived sublattice magnetization is in good agreement with its directly measured counterpart. We also show the usual molecular-field result for these three materials in order to emphasize the quantitative improvement obtainable by means of the susceptibility method presented here over the molecular-field-theory result.

## THEORY

Consider a two-sublattice antiferromagnet with each sublattice containing $\frac{1}{2}N$ identical magnetic ions. For each sublattice we introduce a seperate Cartesian coordinate system $x$, $y$, $z$ and we also define an external Cartesian coordinate system $\xi$, $\eta$, $\zeta$ such that $\zeta$ is *parallel* to the positive $z$ direction of one sublattice (denoted $+$) and *antiparallel* to the positive $z$ axis of the second sublattice (denoted $-$). The magnetization of each sublattice lies in the positive $z$ direction of its own coordinate system, and this will be taken to be the axis of quantization. There is an external magnetic field $H_\zeta$ in the positive $\zeta$ direction.



FIG. 1. Normalized sublattice magnetization $M/M_0$ versus reduced temperature $T/T_N$ for $MnF_2$. (Curve taken from NMR measurements of Refs. 2–6; filled circles show results calculated from $\chi_{||}$ of Ref. 11; empty circles show molecular-field results for $S=\frac{5}{2}$.)
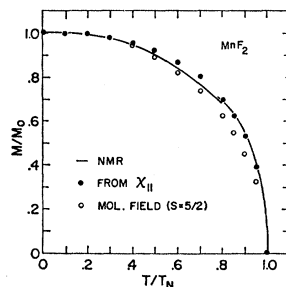
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FIG. 2. Normalized sublattice magnetization $M/M_0$ versus reduced temperature $T/T_N$ for $CuCl_2 \cdot 2H_2O$. (Curve taken from NMR measurements of Refs. 6–8, filled circles show results calculated from $\chi_{||}$ of Ref. 13, empty circles show molecular-field results for $S=\frac{1}{2}$.)
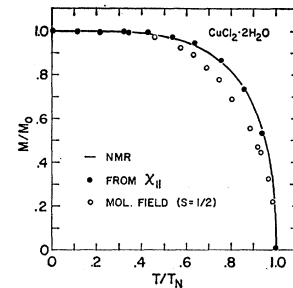
To each magnetic ion we assign the spin Hamiltonian[10]

$$\mathcal{H}^\pm = -g\beta S_z H_z{}^{\text{eff}\pm} - \beta^2 \delta H_\zeta{}^2 + \mathcal{H}_a. \qquad (1)$$

Here we have a Zeeman term due to the effective magnetic field $H_z{}^{\text{eff}\pm}$, a Van Vleck term, and a term independent of the external field (such as crystal anisotropy) $\mathcal{H}_a$. The symbols $g$, $\beta$, and $S_z$ represent, respectively, the spectroscopic splitting factor, the Bohr magneton, and the $z$ component of the electron-spin operator. The constant $\delta$ fixes the magnitude of the Van Vleck term.

Using the method of "thermodynamic perturbation theory," it may be shown[10] that Eq. (1) leads, in the the molecular-field formalism, to the following results for the sublattice magnetization $M$ and the parallel susceptibility $\chi_{||}$:

$$M = \tfrac{1}{2}Ng\beta S B_S(x), \qquad (2)$$

$$\chi_{||} = \frac{(Ng^2\beta^2 S^2/kT)B_S'(x)}{1+(A+\Gamma)(Ng^2\beta^2 S^2/2kT)B_S'(x)} + 2N\beta^2\delta. \qquad (3)$$

Here $A$ and $\Gamma$ are the molecular-field coefficients representing the inter- and intra-sublattice exchange interactions, $k$ is Boltzmann's constant, $T$ is the temperature, $B_S(x)$ is the Brillouin function, and $B_S'(x) = \partial B_S(x)/\partial x$.

We now can, in principle, eliminate $x$ between Eqs. (2) and (3), thus expressing the sublattice magnetization $M$ as a function of $\chi_{||}$, the parallel susceptibility. Since, as shown by Rado,[10] we may write

$$\langle m \rangle = S B_S(x), \qquad (4a)$$

$$\langle m^2 \rangle - \langle m \rangle^2 = S^2 B_S'(x), \qquad (4b)$$

we see that this elimination of $x$ amounts to writing $\langle m^2 \rangle$ as a function of $\langle m \rangle$. (Here $\langle \ \rangle$ denotes an average over a canonical ensemble and $m$ the $S_z$ quantum number.) From the results of Callen and Shtrikman[1] it thus seems reasonable that the relation between $M$ and $\chi_{||}$ should have a greater range of validity than the molecular-field equations from which it was derived.

## APPLICATIONS

We have used the method of the preceeding section to calculate the sublattice magnetization of the antiferromagnets $MnF_2$, $CuCl_2 \cdot 2H_2O$, and $FeF_2$.

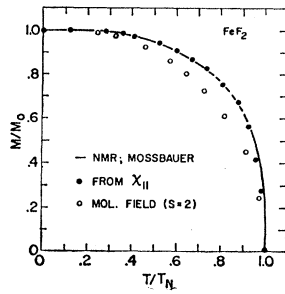[10] G. T. Rado, Phys. Rev., **128**, 2546 (1962).

FIG. 3. Normalized sublattice magnetization $M/M_0$ versus reduced magnetization $T/T_N$ for FeF$_2$. (Curve taken from NMR and Mossbauer measurements of Refs. 6 and 9; filled circles show results calculated from $\chi_{||}$ of Ref. 15; empty circles show molecular-field result for $S=2$.)

For the case of MnF$_2$, we have calculated $M$ from the measured $\chi_{||}$ of Foner.[11] The combined Van Vleck–diamagnetic contribution at $T=0°K$ of about[12] $2\times10^{-7}$ emu/g is negligible. Taking the Néel point at the temperature at which $\chi_{||}$ is maximum gives $T_N=72°K$ and $\Delta=109°K$, where

$$\Delta=Ng^2\beta^2 S(S+1)(A+\Gamma)/6k, \qquad (5)$$

with, for Mn$^{++}$, $S=\frac{5}{2}$ and $g=2.0$. The results for the $\chi_{||}$-derived sublattice magnetization are shown in Fig. 1, together with the NMR results[2–6] and the molecular-field curve for $S=\frac{5}{2}$. All results have been normalized to the same $T_N$. It is clear from Fig. 1 that the susceptibility-derived results are in excellent agreement with the direct NMR measurements. The maximum deviation of the $\chi_{||}$-derived magnetization from the NMR curve in the range $0<T/T_N<0.9$ is 2% of $M_0$, while that of the molecular-field magnetization is 9%.

For the case of CuCl$_2\cdot$2H$_2$O, we have calculated $M$ from the measured $\chi_{||}$ of Van der Marcel et al.[13] Here again, the combined Van Vleck–diamagnetic contribution is negligible. We find, from the single-crystal measurements of Van der Marcel et al.,[13] that the Néel point is at $T_N=4.65°K$. Using Eq. (5) with $S=\frac{1}{2}$ for Cu$^{++}$ and $g=2.2$,[14] we find $\Delta=8.65°K$. The results for the $\chi_{||}$-derived sublattice magnetization are shown in Fig. 2, together with the NMR results[6–8] and the molecular-field curve for $S=\frac{1}{2}$. Again, all results have been normalized to the same $T_N$. As in the case of MnF$_2$, the susceptibility-derived magnetization of CuCl$_2\cdot$2H$_2$O is in excellent agreement with the results obtained by direct NMR measurements. The maximum deviation of the $\chi_{||}$-derived magnetization from the NMR curve, in the range $0<T/T_N<0.9$, is 2% of $M_0$, while that of the molecular-field magnetization is 13%.

For the case of FeF$_2$, we have calculated $M$ from the

measured $\chi_{||}$ of Foner.[15] Here there is a significant Van Vleck contribution of approximately $12.5\times10^{-6}$ emu/g, including a small diamagnetic contribution of about $0.5\times10^{-6}$ emu/g. The Néel temperature is taken to be $T_N=80.5°K$. Using $S=2$ for Fe$^{++}$ and $g=2.22$,[15] we find, from Eq. (5), that $\Delta=111°K$. The results for the $\chi_{||}$-derived magnetization are shown in Fig. 3, together with a combination of NMR[6] and Mössbauer-effect[9] measurements of the sublattice magnetization and the molecular-field curve for $S=2$. The NMR results are shown in Fig. 3 for the temperature range $0<T/T_N<0.75$ and the Mössbauer results for the temperature range $0.9<T/T_N<1.0$. We have joined the two curves since Wertheim has reported[9] that his results are in agreement with the NMR measurements at lower temperatures. As previously, we have normalized all results to the same $T_N$ and, as previously, we find excellent agreement between the $\chi_{||}$-derived $M$ and the directly measured $M$. The maximum deviation of the $\chi_{||}$-derived magnetization, in the range $0<T/T_N<0.9$, is 1.5%, while that of the molecular-field magnetization is 14%.

## DISCUSSION

We have shown, in the previous section, that excellent results for the sublattice magnetization of the antiferromagnets MnF$_2$, CuCl$_2\cdot$2H$_2$O, and FeF$_2$ may be obtained from the experimentally measured parallel susceptibility. The reason for using the parallel susceptibility for this purpose, rather than, for example, the perpendicular susceptibility or powder measurements, is that there would then appear other terms in Eqs. (2) and (3) and our resulting expression for the susceptibilities would have a greater dependence on the exact form of $H_0$. This dependence is shown, in the molecular-field approximation, by the results of Honma.[16,17]

We have applied the methods discussed here to derive the sublattice magnetism for Cr$^{+++}$ in Cr$_2$O$_3$ from the $\chi_{||}$ measurements of Foner.[18] Using this result, we have examined the magnetoelectric effect in Cr$_2$O$_3$[19] and have been able to make a more accurate assessment of the extent of the contributions of various mechanisms to the magnetoelectric susceptibility than has been possible using the molecular-field theory.[10] In making this assessment, the technique of deriving the sublattice magnetization from available $\chi_{||}$ measurements has proved extremely useful. The results shown here for MnF$_2$, CuCl$_2\cdot$2H$_2$O, and FeF$_2$ indicate that this method provides accurate results for the sublattice magnetization within the spin-Hamiltonian formalism.

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