

ert see this decrease for only one and one-half decades may be that the rapidly increasing lattice resistivity takes over at about 20°K, and that the applicability of Matthiessen's rule is rather in doubt in these circumstances.)

The works of Abrikosov and of Suhl were based on perturbation theory and on scattering theory, respectively. The essential equivalence of the two approaches has been explicitly demonstrated by Silverstein and Duke.⁵ Nagaoka's approach⁶ was based on equations of motion of Green's functions combined with a truncation procedure. He obtained results valid above and below T_c and interpolated between them in the intervening range. A fresh assessment of this method was recently made by Hamann⁷ who essentially succeeded in demonstrating the equivalence of all three methods. He concluded that the truncation method probably relates to the other two in the same way as the random-phase approximation in certain many-body problems relates to diagram summation techniques. Using a specially simple model (zero-range coupling, no ordinary potential scattering), Hamann is able to exhibit the solution in explicit form. However, this neglect of potential scattering is serious, since the calculation of the total amplitude couples spin-

flip and spin-nonflip potential in an essential way⁴ [e.g., T_c is sensitive to the ordinary potential, the formula $T_c \sim \epsilon_F \exp(-\epsilon_F/J)$ being valid only for very small potential V]. On the other hand, Ref. 4 indicates that the low-temperature plateau value of the resistivity is only weakly dependent on V .

To summarize, it appears that the resistivity measurements of Daybell and Steyert furnish evidence for the essential correctness of the analytic continuation procedure of the Born series solution from $T > T_c$ to $T < T_c$. Also, theoretical progress made since publication of Refs. 2 and 3 indicates that all three approaches are rapidly converging to the same result.

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PARAMAGNETIC RESONANCE IN AN EXCITED STATE OF TmN: CRYSTAL-FIELD AND EXCHANGE EFFECTS

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Paramagnetic resonance has been observed in an excited Γ_5 triplet state 222°K above the singlet Γ_1 ground state of Tm^{3+} ($4f^{12}$) in TmN (NaCl structure). Much of the observed behavior is understood with exchange small compared with crystal-field effects; however, there is an anomalous minimum in the temperature variation of the resonant g .

Paramagnetic resonance has been observed for temperatures between 77 and 240°K in a thermally populated Γ_5 triplet excited state 222°K above the singlet ground state of Tm^{3+} ($4f^{12}$) in cubic TmN (i.e., pure compound concentrated in Tm^{3+}). Since Tm^{3+} in a cubic environment has two excited states of Γ_5 symmetry, the one whose resonance is observed

and another about 400°K higher in energy for TmN, the Γ_5 wave functions vary with the ratio of fourth- to sixth-order crystal-field strength. This in turn means that the g factor for either Γ_5 level is a sensitive measure of this ratio. The experimentally observed g factor has a small temperature dependence and lies slightly above the value for a fourth-order-only crys-

tal field. For small Heisenberg exchange, theory predicts a g shift from the crystal-field-only value approximately proportional to the dc susceptibility. The over-all trend of the experimental g temperature dependence is consistent with this for small ferromagnetic exchange (about 15% of the critical value necessary¹ for magnetic ordering). (The small magnitude of exchange is consistent with the lack of magnetic ordering¹⁻⁴ and the observed Van Vleck-type susceptibility²⁻⁴ for TmN. The fact that exchange is ferromagnetic is consistent with the fact that the nitrides of Gd through Er, which do order,¹ are ferromagnetic.) However, there is an anomalous minimum in the g temperature dependence centered about 120°K. The intensity reaches its maximum and the linewidth a minimum near the same temperature. The analysis of the behavior of g , ignoring the anomaly, yields values for the crystal-field and exchange parameters. These crystal-field parameters give a calculated temperature dependence of the resonant intensity in quite good agreement with experiment.

The lack of magnetic ordering¹ and Van Vleck-type susceptibility²⁻⁴ for TmN (NaCl structure) can be understood when crystal-field effects are dominant over exchange, and the crystal-field ground state is a singlet as shown in Fig. 1. It is interesting to study paramagnetic resonance^{4,5} in excited states of TmN both in order to determine the crystal-field and exchange parameters necessary for a quantitative understanding of the macroscopic magnetic properties, and also in the hope that further understanding

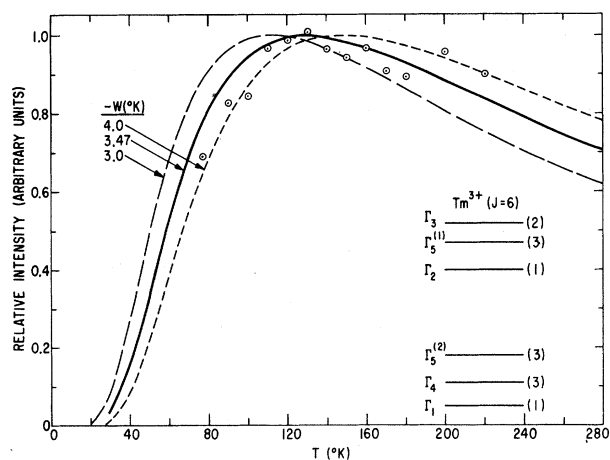


FIG. 1. Temperature dependence of intensity of $\Gamma_5^{(2)}$ resonance. Crystal-field level scheme for Tm^{3+} shown in lower right.

of the microscopic interactions and dynamic effects may result from the detailed study of the behavior of a single state.

The octahedral crystal field is specified⁶ by two parameters: x , giving the ratio of fourth- to sixth-order terms, and W , giving the absolute scaling of the energy-level separations. (The ordering of levels shown holds for $-1 \leq x \leq -0.55$. As x varies within this range, the relative splittings of the levels change.⁶ For $x \geq -0.55$, there are level crossings, and the Γ_1 and Γ_4 states are no longer the two lowest lying states for Tm^{3+} . Susceptibility and magnetization measurements²⁻⁴ on TmN and the other Tm compounds of NaCl structure with group-V anions require x to lie in this range.) The resonant g for the Γ_4 level is independent of x and $g_4 = 0.5833$. Since there are two Γ_5 levels, the g 's for those levels vary strongly with x . For example, g for $\Gamma_5^{(2)}$ has its maximum value of 2.212 at $x = -1$ and already decreases to 1.92 for $x = -0.90$. As x varies toward 0, g decreases further monotonically to 0.05 for $x = -0.4$. For $x > -0.4$, g increases but only to a value of 0.51 at $x = 0$. Thus, paramagnetic resonance for the Γ_5 triplet determines x . The temperature dependence of the intensity is quite distinctive and depends on W . This is illustrated in Fig. 1 for three values of W (for $x = -1$) spanning the range of values possible for consistency with the susceptibility allowing for ambiguity in the role of exchange. The magnetic field available restricted the present in-

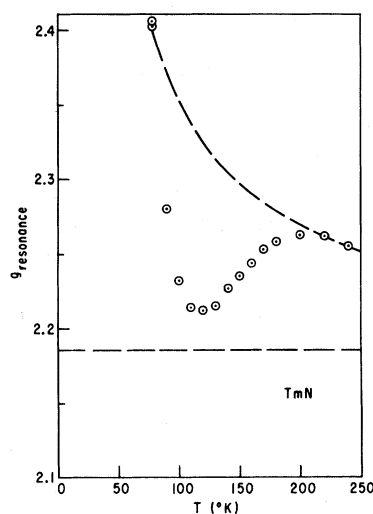


FIG. 2. Temperature dependence of resonant g factor. Curve of $1/T$ dependence shown with asymptotic limit at $g = 2.186$.

vestigation to the $\Gamma_5^{(2)}$ resonance.

Paramagnetic resonance was observed at frequencies near 9.35 Gc/sec for a 152.5-mg powdered sample of TmN. The sample was sealed in a Pyrex tube under argon, but even then the sample deteriorated slowly over a time period of months.

The experimental recordings are the usual derivatives of absorption. A double integration was performed with a planimeter to find the intensities shown in Fig. 1. The resonant g shifted with temperature as shown in Fig. 2. It is striking that g has a minimum at about the same temperature as the intensity maximum. The peak-to-peak derivative linewidth varies between 400 and 450 G and has a minimum at

approximately the same temperature as the g minimum. As the temperature of maximum intensity is approached, the line shape approaches the Lorentzian line shape expected for extreme narrowing.

Theoretically, for crystal-field effects only, the g is temperature independent and has a maximum value of $g = 2.212$ at $x = -1$ (fourth-order anisotropy only). The experimental g has a minimum value of 2.212 at 120° , and for other temperatures, slightly exceeds the maximum possible crystal-field-only g value. We have examined to what extent this behavior can be understood by the presence of a small ferromagnetic Heisenberg exchange. By a moment calculation,⁷ the mean frequency of resonant absorption is

$$\langle h\nu \rangle = g_5^{(2)}\beta H + 2\mathcal{J}(0)\langle \Gamma_{5a}^{(2)} | J_z | \Gamma_{5a}^{(2)} \rangle \{ \langle J \rangle - (\lambda\beta H/kTZ) \langle \Gamma_{5b}^{(2)} | J^- | \Gamma_{5a}^{(2)} \rangle^2 \exp[-E(\Gamma_5^{(2)})/kT] \}. \quad (1)$$

Here $g_5^{(2)}$ is the crystal-field-only value, $\mathcal{J}(0) = \sum_i \mathcal{J}_{ij}$ is the total exchange interaction per ion with all neighbors, and Z is the single-ion crystal-field partition function. The lower, middle, and upper Zeeman split $\Gamma_5^{(2)}$ states are labeled a , b , and c , respectively. In (1), $\langle J \rangle$ is the thermal average angular momentum per ion for vanishing exchange and is directly proportional to the susceptibility.

For TmN there are two contributions to the susceptibility. One contribution, χ_R , is the part of the susceptibility arising from the population difference caused by a magnetic field between states having a permanent moment in the absence of a magnetic field. The second contribution, χ_b , comes from that part of the moments of the states that is induced by the field. For TmN, χ_b accounts⁴ for 95% or more of the total susceptibility. In (1), the second subtractive term in the braces cancels that part of the susceptibility coming from the $\Gamma_5^{(2)}$ part of χ_R . Curiously enough, the maximum subtraction occurs at about the same temperature as the minimum in the g value. Nevertheless, to a good approximation, $\langle h\nu \rangle$ is proportional to χ . Higher order exchange effects, secular or nonsecular, do not change this conclusion.⁷

We adopt the point of view that a shift in g proportional to the susceptibility will explain the over-all trend of the g temperature dependence, while it does not explain the anomalous minimum. For the temperatures of interest

χ is given to a good approximation by a Curie law.⁴ For $\mathcal{J}(0)J(J+1) = 11.4^\circ\text{K}$, the g values at 77, 220, and 240°K fall on the $1/T$ curve shown in Fig. 2 which approaches the asymptotic value $g = 2.186$ giving $x = -0.990$. Unfortunately, it is difficult to extend our measurements to lower or higher temperatures for signal and noise reasons.

From molecular field theory the value of the susceptibility at 0°K gives $W = -3.47^\circ\text{K}$. We use these values of x and W to calculate the intensity shown in Fig. 1, which is in good agreement with experiment. The basic correctness of our analysis, apart from the g anomaly, is supported both by the fact that the experiments and our analysis give a value of W falling in the middle of the range of values admitted by susceptibility measurements and by the good agreement with the theoretical intensity for the $\Gamma_5^{(2)}$ resonance.

As pointed out above, the crystal-field-only g is extremely sensitive to x . In our scheme of analysis, the experimental high-temperature asymptotic value of g gives this crystal-field-only value. Putting aside any detailed theoretical arguments about the temperature variation of g , it would require the experimental g to fall off very sharply for temperatures higher than those measured to get a crystal-field-only g corresponding to any appreciable amount of sixth-order anisotropy. For example, a value for x of -0.60 would require the high-

temperature limiting value of g to be 0.65, rather than 2.186 as indicated above, and g is even smaller for smaller $|x|$.

As a gauge for the size of crystal-field effects found, we have done a point-charge calculation for x and W . The point-charge model gives $x = -0.963$, while the value of W found here would require 25.9 electronic charges per nitrogen site. Thus, the point-charge model is consistent with an almost completely fourth-order crystal field. However, the charge required is an order of magnitude greater than that for any simple ionic model. The close agreement of the point-charge value of x with experiment may be coincidental. Experiments on rare earths in alkali earth halides⁸ and ThO₂⁹ give results for x at variance with point-charge calculations. On the other hand,¹⁰ Er³⁺ in ZnSe gives surprisingly good agreement with point-charge calculations for $A_4\langle r^4 \rangle$ and $A_6\langle r^6 \rangle$.

The fact that the crystal field deduced from the experimental g value is so close to completely fourth-order is quite interesting. The question of the relative importance of fourth- and sixth-order crystal-field contributions has aroused much interest. The work of Elliott and Stevens¹¹ on ethyl sulfates and of Judd¹² on double nitrates found that the sixth-order terms, in particular $V_6^8 = A_6^6\langle r^6 \rangle$ for ethyl sulfates and V_6^6 and $V_6^3 = A_6^3\langle r^6 \rangle$ for double nitrates, are dominant. This was in distinction to earlier speculation that sixth-order terms would be negligible. This led to much discussion. The most thorough theoretical discussion of the various shielding and antishielding effects involved is that of Freeman and Watson.¹³ The problem is quite complex, and even Freeman and Watson were forced to neglect many important effects. It is striking that typically in cubic materials (e.g., rare earths^{14-16,10} in alkali earth halides, MgO, CaO, ZnSe) in contrast to lower symmetry environments the fourth-order contribution is dominant, i.e., $A_4\langle r^4 \rangle \gg A_6\langle r^6 \rangle$. Usually the dominance of fourth-order terms is not so complete as in TmN. Typically $|x|$ falls between 0.4 and 1. The fact that TmN is metallic also complicates comparison with theoretical ideas such as those of Freeman and Watson.

The various effects discussed in this note do not explain the anomalous minimum in g . The subtractive term in (1) has the tempera-

ture dependence of the intensity, and thus has a maximum near the temperature of the g minimum. However, it is too broad and, more importantly, much too small to give the g minimum. The possibility should be kept in mind that the exchange mechanism itself may depend on the symmetry of the occupied states of the two interacting localized spins, so that no simple representation such as a Heisenberg form is adequate.

There is one experiment that would greatly clarify the nature of the exchange g shift. This would be observation of the Γ_4 resonance. Since the g for that level is independent of x , one could unambiguously identify the shift from the octahedral crystal-field value.

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