

Spin-Wave Scattering of Phonons in Antiferromagnets

R. E. NETTLETON*

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York

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The matrix elements calculated by Upadhyaya and Sinha⁵ for one-phonon interactions with spin waves have been used to calculate the phonon relaxation time. It is found that for wave number q , $\tau_q^{-1} \propto Tq^4$. For such a Rayleigh-type scattering, coupled with contributions from external boundaries and point defects, the thermal-conductivity integral can readily be evaluated exactly in the approximation of isotropic, acoustic phonons, and for temperatures much less than the Debye temperature. The resulting analytic expression has been fitted to measurements by Slack on single crystals of MnF_2 , CoF_2 , and MnO . A very good fit is found only for MnF_2 , for which experiment and theory agree from 0°K to the maximum at 14.7°K where three-phonon processes take over. In CoF_2 , high impurity content led to low-temperature resonances, and agreement was found only at the lowest temperatures and near the maximum. The magnetic fitting parameter obtained in this way, however, agrees as to order-of-magnitude with theoretical estimates. In MnO , agreement was poor and few conclusions could be drawn.

1. INTRODUCTION

FOLLOWING the lead of Akhieser,¹ there have been several treatments^{2,3} of the scattering of phonons by spin waves in ferromagnets. These papers conclude: (1) The dominant spin-lattice interaction term in the crystal Hamiltonian arises from the electron-electron exchange coupling, rather than from spin-orbit coupling; and (2) one-phonon processes, in which a magnon is scattered and a phonon created or absorbed, dominate over two-phonon processes.

Despite these important advances, the above-mentioned theories have found no direct application to the analysis of thermal conductivity measurements. The reason for this is undoubtedly that in iron and nickel, for which most conductivity measurements have been made,^{4a,b} the electron contribution is predominant and difficult to separate from the phonon component. Consequently, the existing theoretical treatments^{2,3} have stopped with a calculation of the equilibration time for the spin and lattice temperatures, which has not been measured.

In dealing with antiferromagnetic dielectrics, however, we need not consider the electronic component of heat conduction. Therefore, we can easily apply the theory recently proposed by Upadhyaya and Sinha⁵ to existing measurements by Slack.^{6a} The theory assumes that magnetic ions are arranged on two interpenetrating simple cubic lattices and that spin-phonon interaction

results from lattice-wave perturbation of the crystal field acting on an electron. From the resulting phonon transition probabilities, we shall calculate in the following section the first two terms in the expansion of the phonon relaxation frequency in powers of the wave number. We shall then go on to insert this relaxation frequency into the thermal conductivity integral, which can be evaluated by contour integration if we assume only point defects and external boundary scattering. The analytic expression thus obtained will be fitted in Sec. 4 to Slack's measurements on MnF_2 , CoF_2 , and MnO . The conclusions which may be drawn from our ability to fit theory and experiment in various temperature intervals below the Néel temperature will be discussed in Secs. 4 and 5.

2. RELAXATION TIME

Upadhyaya and Sinha⁵ have calculated the matrix elements for one-phonon transitions which, as in earlier work on ferromagnets^{2,3} are thought to be dominant over two-phonon processes. The interaction Hamiltonian used in this calculation, which arises from exchange forces, was expressed in terms of phonon and spin-wave creation and annihilation operators through the formalism of Holstein and Primakoff,⁷ which limits the results to low temperatures, where the operator expansions can reasonably be expected to converge. The matrix elements, and the transition probabilities obtained by squaring them, are thus proportional to phonon and magnon occupation numbers [Ref. 5, Eqs. (3.1)–(3.3)]. Since no magnon component of heat flux is observed experimentally,^{6a} and since magnons are important as phonon scatterers only near the conductivity maximum where any low-temperature ($\sim 1^\circ K$) spin-wave heat current will normally have disappeared,^{6b} we may suppose that the spin waves have such a short relaxation time that we can legitimately express the magnon occupation numbers by an equilibrium Bose distribution. When this is done, the fluctuations

* Visiting Fellow, 1963. Present address: National Bureau of Standards, Washington, D. C.

¹ A. Akhieser, *J. Phys. (USSR)* **10**, 217 (1946).

² M. I. Kaganov and V. M. Tsukernick, *Zh. Eksperim. i Teor. Fiz.* **36**, 224 (1959) [English transl.: *Soviet Phys.—JETP* **9**, 151 (1959)].

³ K. P. Sinha and U. N. Upadhyaya, *Phys. Rev.* **127**, 432 (1962).

⁴ (a) W. R. G. Kemp, P. G. Klemens, and G. K. White, *Australian J. Phys.* **9**, 180 (1956). (b) W. R. G. Kemp, P. G. Klemens, and R. J. Tainsh, *Ann. Physik* **5**, 35 (1959).

⁵ U. N. Upadhyaya and K. P. Sinha, *Phys. Rev.* **130**, 939 (1963).

⁶ (a) G. A. Slack, *Proceedings of the International Conference on Semiconductor Physics* (Czechoslovak Academy of Sciences, Prague, 1961), pp. 630–633. (b) R. L. Douglass, *Phys. Rev.* **129**, 1132 (1963).

⁷ T. Holstein and H. Primakoff, *Phys. Rev.* **58**, 1098 (1940).

$n_q = N_q - N_q^0$, of the phonon occupation numbers from equilibrium, obey a Boltzmann transport equation with a relaxation time τ_q which is a function of the wave number (and polarization index, which is understood, and not written explicitly).

Since the analysis is necessarily restricted to low temperatures by the domain of validity of the spin-wave theory, we should be able to effect a straightforward expansion of τ_q^{-1} in powers of wave number q . This has been done, starting with Eqs. (3.1)–(3.3) and (3.11) of Ref. 5 and using the acoustic phonon approximation $\omega_q = cq$. We shall give only the result, since the details have no intrinsic interest. If we define $\theta_D \equiv \hbar c/\kappa a$, where c = sound velocity; a is the lattice parameter; κ = Boltzmann's constant; and also $\theta_c \equiv \epsilon_k/\kappa a$, where ϵ_k is the energy of a magnon of wave number k , then the Taylor expansion of τ_q^{-1} depends on the ratio $\theta_c/\theta_D \equiv p$. Specifically, we have

$$1/\tau_q = \alpha_4 q^4 + \alpha_6 q^6 + O(q^7) (\theta_c < \theta_D), \quad (1)$$

where

$$\alpha_4 = \frac{4V\hbar^2 c S^2 (\alpha J)^2}{\pi N M \kappa^2 \theta_c^4 p^4} T (1-p^2)^2 (\tanh^{-1} p - p), \quad (2a)$$

$$\alpha_6 = \frac{V\hbar^4 c^3 S^2 (\alpha J)^2}{36\pi N M \kappa^5 \theta_c^4 p T} (1-p^2)^2. \quad (2b)$$

N denotes the number of atoms of mass M ; S is the spin quantum number for a magnetic ion, and αJ is the derivative of the exchange integral with respect to nearest-neighbor distance [Ref. 5, Eq. (2.8)]. On the other hand, when $\theta_c > \theta_D$, we obtain

$$1/\tau_q = \alpha_3 q^3 + \dots (\theta_c > \theta_D), \quad (3)$$

where

$$\alpha_3 = \frac{8V\pi\hbar S^2 (\alpha J)^2 T^2}{3NM\kappa^2\theta_c^4 p^4} (1-p^2)^2. \quad (4)$$

The q^4 or q^3 dependence of τ_q^{-1} found here differs from ferromagnets, where a similar analysis based on Refs. 2 and 3 leads to τ_q^{-1} proportional to q . The difference arises from the difference in spin-wave dispersion relations.

These expressions for $1/\tau_q$ require correction for temperatures in the liquid He range. Such a correction, which should probably appear as a multiplicative exponential factor in Eqs. (1) or (3), arises from the low-frequency gap in the spin-wave spectrum caused by the anisotropy field. This gap is neglected by Sinha and Upadhyaya,⁵ and we shall continue to neglect it here. For temperatures $\sim 4^\circ\text{K}$, the observed phonon scattering is entirely due to boundaries and nonmagnetic point defects. At temperatures $> 10^\circ\text{K}$, where magnon scattering should become observable, any effect produced by the magnon energy gap will be greatly diminished and probably cannot be observed.

Whether we use Eq. (1) or Eq. (3) depends on an

estimate of θ_c , which can be made only crudely. Following the procedure of Landau and Lifshitz,⁸ we shall assume that the spin-spin energy is $\sim -\kappa T_N$ when the spin system is completely ordered (T_N = Néel temperature). Thus if J is the exchange integral and z the lattice co-ordination number,

$$zJS^2 \cong \kappa T_N.$$

Since [Ref. 5, discussion following Eq. (3.6)],

$$\kappa\theta_c = 2JS(2z)^{1/2},$$

we have

$$\theta_c = T_N/S$$

for a bcc lattice with $z=8$. With $S \sim \frac{5}{2}$, the condition $\theta_c < \theta_D$ should be satisfied if T_N is less than the Debye temperature, which should be of order θ_D . For MnF_2 , CoF_2 , and MnO , the condition $\theta_c < \theta_D$ is clearly satisfied, while for NiO and CoO a reasonable choice of a leads to $\theta_c > \theta_D$ even though θ_c is less than the Debye temperature. Such a contradiction makes it appear that the model is too unrealistic, and its application highly uncertain, and so attention here will be centered on substances for which (1) obtains, and we shall make no use of (3).

To the q^4 Rayleigh scattering produced by spin waves, one should add a similar contribution from mass defects and strain fields produced by impurities⁹ to give a total relaxation time

$$1/\tau_q = (P + QT)q^4 \quad (5)$$

with P and Q constants, of which the latter can be calculated from Eq. (2a).

3. THERMAL CONDUCTIVITY INTEGRAL

Because αJ and thus Q can be estimated at best only to a given order-of-magnitude, we are at present able to draw no theoretical conclusions from an attempt to distinguish between longitudinal and transverse phonons. This distinction will therefore be abandoned. Further, we shall assume isotropic crystals, since this is a good approximation for low temperature¹⁰ in MnF_2 and CoF_2 .

With these approximations, together with acoustic phonons, the reduced thermal conductivity K_r' is given (in dimensions of sec) by [cf. Ref. 9, Eq. (3.34)]:

$$K_r' \equiv K [(2\pi^2 \hbar^3 c) / (\kappa^4 \theta_D^3)] \\ = y^2 \int_0^1 d\xi \xi^4 e^{\xi y} \tau(\xi) / (e^{\xi y} - 1)^2, \quad (6)$$

where K is the thermal conductivity, $y = \Theta_D/T$ for Θ_D the experimental Debye temperature, and the relax-

⁸ L. Landau and E. Lifshitz, *Physik. Z. Sowjetunion* 8, 153 (1935).

⁹ P. Carruthers *Rev. Mod. Phys.* 33, 92 (1961); see Eq. (6.2).

¹⁰ G. A. Slack, *Phys. Rev.* 122, 1451 (1961).

TABLE I. Reducing and fitting parameters used in analyzing experiments of Slack. c =sound velocity; L =crystal diameter; a =lattice parameter; T_N =Néel temperature; S =spin of magnetic ion; θ_c =characteristic temperature of magnon dispersion relation; θ_D =characteristic temperature of phonon dispersion relation; Θ_D =approximate low-temperature Debye Θ ; β =multiplier for boundary scattering; A =point-defect fitting parameter; B =fitting parameter for magnon scattering; ${}^a J$ =derivative of exchange integral with respect to nearest-neighbor distance.

Sub- stance	$10^{-5} c$ cm/sec	L cm	$10^8 a$ cm	T_N °K	S $\frac{h}{2\pi m_0 c}$	θ_c °K	θ_D °K	Θ_D °K	β	$10^{-4} A$	$10^{-5} B$	$10^7({}^a J)$ dyn
MnF ₂	3.0	0.13	2.573	67	5	26.8	89.1	450	5.4515	1.43	6.10	0.0487
CoF ₂	2.9	0.13	2.476	35	5	23.3	89.4	450	49.58	8.259	47.31	0.4764
MnO	1.7	0.5	2.417	120	5	48	53.7	230	10	69.93	846.73	4.285

ation frequency

$$1/\tau(\xi) = \beta(c/L)[1 + (A + By^{-1})\xi^4], \quad (7)$$

$\xi \equiv \hbar c q / \kappa \Theta_D$.

The term $\beta c/L$ arises from scattering due to external boundaries, if L is of the order of the specimen diameter. β should be ~ 1 , though in the specimens analyzed here we shall find it ~ 10 . The constant B is given in terms of Q [in Eq. (5)] by

$$B = Q(L/\beta c) \Theta_D (\kappa \Theta_D / \hbar c)^4.$$

For $T < T_N$, y is sufficiently large so that we can take the upper integration limit in (6) to be ∞ . With this further approximation, the integral can be evaluated exactly by contour integration to give

$$\begin{aligned} K_r &\equiv \beta(c/L) K_r' \\ &= -(\pi/2) \alpha y^{-3} m e^m [\cos m + \sin m + e^{2m} (\cos m \\ &\quad - \sin m) - 2e^m] [e^{2m} - 2e^m \cos m + 1]^{-2} \\ &\quad + 4\pi \alpha^2 y^{-3} \sum_{n=1}^{\infty} (2\pi n)^3 / [\alpha + (2\pi n)^4]^2 - \frac{1}{2} \alpha y^{-3}, \end{aligned} \quad (8)$$

where

$$\begin{aligned} \alpha &\equiv y^4 [A + By^{-1}]^{-1} \\ m &\equiv \alpha^{1/4} 2^{-1/2}. \end{aligned}$$

For $T > 10^\circ\text{K}$, the middle term in the right-hand member of (8) can be approximated by

$$\begin{aligned} &(\alpha^2 y^{-3}) / (8\pi^4) \{ [1 + \alpha / (2\pi)^4]^{-2} + 0.0369 \\ &\quad - 4.016 \times 10^{-3} [\alpha / (2\pi)^4] + 3.681 \times 10^{-4} [\alpha / (2\pi)^4]^2 \\ &\quad - 3.056 \times 10^{-5} [\alpha / (2\pi)^4]^3 + \dots \}. \end{aligned}$$

Inspection of Eq. (8) shows that K_r is a function of $\zeta^{-1} \equiv A + By^{-1}$. Therefore, in order to determine A and B to fit a given set of empirical data, we choose a value of y and then vary ζ until the calculated K_r coincides with the experimental value. To do this, of course, one must first choose a value of β , which can usually be done by fitting K_r to the experimental value at $T \sim 1^\circ\text{K}$, where point defects can be neglected. When a table of values $\zeta(y_i)$, chosen to fit the data at the corresponding temperatures, has been built up, we must have $\zeta(y_1) > \zeta(y_2)$ if $y_1 > y_2$. When this condition is not satisfied over a range of three or more data points, we may con-

clude that it is impossible to fit both magnitude and slope in the given temperature range and that for this set of data points some other mechanism must be assumed beside boundary and point-defect scattering. In the calculations to be reported in the following section, the parameters A and B were adjusted to fit those regions near the conductivity maximum where $\zeta(y)$ increased with y . This leaves large temperature ranges where no fit seems possible unless we take A or B to have an unphysical negative value. Possible phonon scattering mechanisms for such regions will be proposed.

4. RESULTS

The fitting procedure described above has been applied to measurements by Slack on single crystals of MnF₂,¹¹ CoF₂,¹² and MnO.¹³ Investigation has been limited to the range $0 < T < T_N$ and stops at 84°K in MnO, since the spin-wave theory should be valid only at very low temperatures, near the conductivity maximum. The parameters used in reducing the data to dimensionless form and in calculating θ_c are listed in Table I. Values of c , T_N , Θ_D , and L have been taken from Slack's papers.^{10,13} The lattice parameter a has been estimated as the nearest neighbor distance in a bcc lattice having the same volume per atom as the lattice here investigated. Most of these values are only approximate, but so long as they are of the correct order of magnitude, our ability to fit the data and the conclusions we draw do not depend on their precise values. The fitting parameters and ${}^a J$ values calculated from them are also listed in Table I. We shall take up each specimen in turn and comment on the fit obtained.

MnF₂

By fitting Eq. (8) at two temperatures on the low-temperature side of the maximum at 14.7°K , it has proved possible to fit all measured values of K between 0°K and the maximum within 4.3%, which is within the experimental error of $\pm 5\%$. This fit has been achieved without the exponential correction for the spin-wave

¹¹ Reference 10, Run No. 18. The author is indebted to Dr. Slack for supplying his data in tabular form for all three crystals studied here.

¹² Reference 10, Run No. 45.

¹³ G. A. Slack and R. Newman, Phys. Rev. Letters **1**, 359 (1958). Run No. 8.

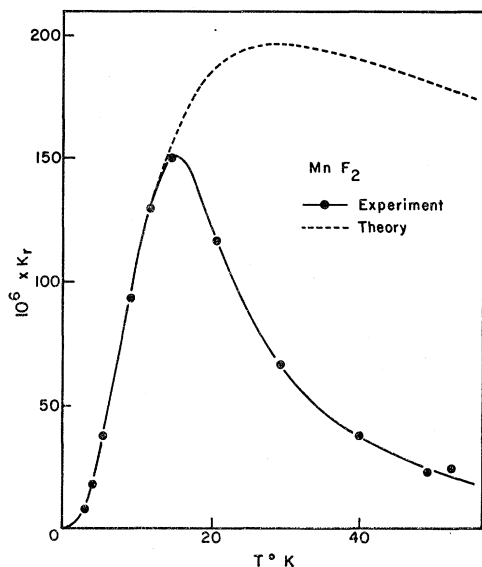


FIG. 1. Experimental points (filled circles) and theoretical fit (dashed curve) using parameters in Table I. Slack's measurements, Ref. 10, Run No. 18, on MnF_2 .

gap which was mentioned in the previous section as being required at He temperature. At the latter temperature, the boundary scattering plus a small contribution from mass defects and strain fields predominates so heavily that the spin-wave effects are all but unobservable. Magnons, in fact, can be seen only through their effect on the thermal conductivity curve over an interval of about 5°K on the low-temperature side of the maximum. Elsewhere, they appear to be masked by other mechanisms.

Beyond the maximum, the theoretical curve (dashed curve in Fig. 1) continues to rise to a peak near 29.3°K . Since this is not near T_N , and since we are concerned with temperatures $\ll \Theta_D$ (cf. Table I), the only mechanism which immediately presents itself to account for the observed scattering above the maximum is three-phonon N processes. Associated with the apparent failure of spin-wave scattering to fit the observed conductivity at higher temperatures, we should recall the absence of a characteristic dip in heat conduction at T_N . Both these effects point to a very weak spin-phonon coupling, and thus to a small αJ . The latter, estimated for MnF_2 from the fitting parameter B , is one or two orders of magnitude lower than the value found for the other two specimens.

CoF_2

This crystal had a very high impurity content, giving rise to high thermal resistance, even at very low temperatures. Thus it was impossible to fit the observed K_T over any appreciable range of T values on the low-temperature side of the maximum without taking $\beta \sim 70$. With such a high β value, however, no fit would

have been possible at the very lowest temperatures or in the vicinity of the max. This situation indicates strongly the presence of a low-temperature resonance, and so β , A , and B were determined to fit the experimental points within 4.2% at $T=2.93$, 14.13 , and 21.01°K . With the value $\beta=49.58$ thus chosen, it was impossible to match both magnitude and slope of the empirical curve at any other data points on either side of the max. Thus the best that could be done was to make the theoretical and experimental maxima nearly coincide, with agreement at the peak and for $T < 2.9^\circ\text{K}$ (cf. Fig. 2).

Because of this coincidence of the maxima, the three-phonon processes are probably less dominant at higher temperatures than they are in MnF_2 . $T_N=35^\circ\text{K}$ for CoF_2 is so low that the failure of the theory on the high-temperature side of the maximum may be attributed in part to breakdown in the spin-wave picture.

The value of αJ (Table I) estimated from the fitting parameter B and Eq. (2a) is within the range 10^{-8} to 10^{-7} dyn proposed by Upadhyaya and Sinha⁵ on the basis of the exchange-integral calculations of Freeman and Watson.¹⁴ Since the order of magnitude of B proves insensitive to adjustments in A and β , the agreement between theoretical and experimental estimates of this parameter is probably better than accidental.

MnO

In this crystal, K is anomalously low at all temperatures studied. If an attempt is made to fit the experimental value at $T=3.48^\circ\text{K}$ assuming scattering by

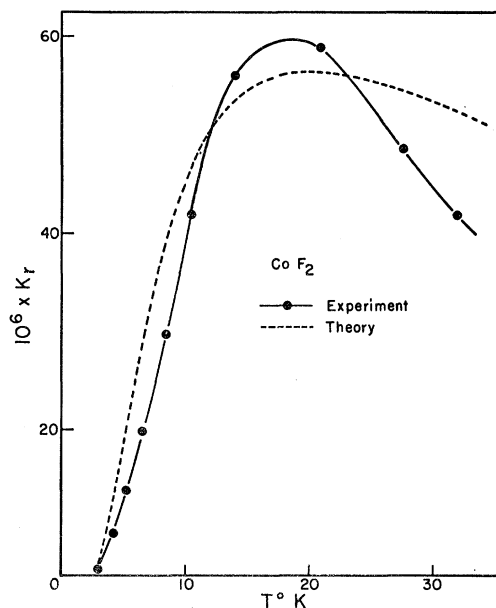


FIG. 2. CoF_2 . Measurements by Slack, Ref. 10, Run No. 45. Fitting parameters for dashed curve listed in Table I.

¹⁴ A. J. Freeman and R. E. Watson, Phys. Rev. **124**, 1439 (1961).

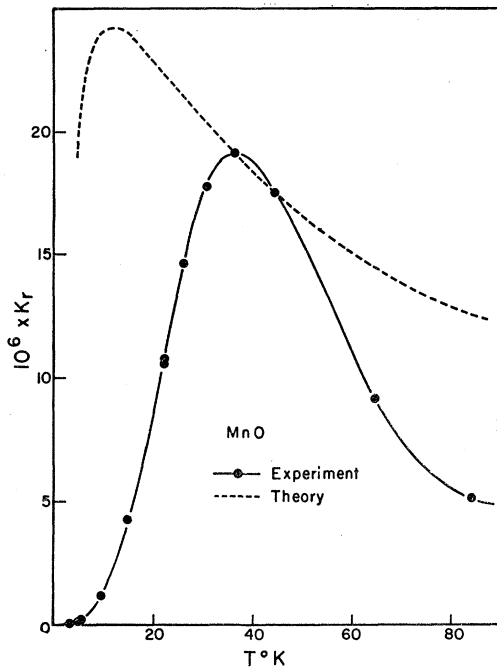


FIG. 3. MnO. Measurements by Slack and Newman, Ref. 13, Run No. 8. Fitting parameters for dashed curve listed in Table I.

external boundaries alone, we get $\beta = 2.6 \times 10^4$. Furthermore, it is impossible to match the magnitude and slope in any other part of the experimental curve. With $\beta \sim 10^4$ at $T = 3^\circ\text{K}$, the theoretical K_r is too low just below the maximum, indicating that the magnitude of the anomalous scattering decreases with temperature. Thus we can suppose that dislocations, which contribute a term $\propto q$ to τ_q^{-1} , are not responsible. It is possible that the sample contained colloidal precipitates of Mn_3O_4 .¹⁵ However, since little is definitely known about the structure or preparation of the crystal, further speculation is probably unprofitable.

Since the anomalous low-temperature scattering decreases with T , it was decided to set $\beta = 10$ (a reasonable value) and determine what kind of fit could be made. The dashed curve in Fig. 3 shows that one can fit a ten-degree interval starting at the maximum, although elsewhere no fit is possible. One might also fit a slightly broader region including the maximum, if one assumes the highest experimental point to be somewhat too high. The slope of the theoretical curve obtained in this way, however, nowhere approximates that of the experimental curve. The value of B obtained from the fit

¹⁵ G. A. Slack (private communication).

shown in Fig. 3 yields a αJ two orders of magnitude greater than that for MnF_2 (Table I). Such a stronger interaction in MnO is in accord with our observation of a dip in K at T_N for this crystal, and our failure to see such a dip in MnF_2 . Because of the over-all poorness of the fit, however, any conclusions we attempt to draw are perilously speculative.

5. DISCUSSION

Because the spin-wave theory is valid only for small fluctuations from perfect ordering of the spins, as a result of the requirement for convergence of the operator expansions employed, the analysis in no case has been extended to within 5°K of T_N . In the immediate vicinity of T_N a different treatment, such as Kawasaki's model¹⁶ based on critical fluctuations in spin energy density, is required. From the apparent dominance of three-phonon processes at temperatures above the maximum, we can tentatively conclude that spins and other point defects determine the slope of the K vs T curve only on the low-temperature side of the maximum and within 1 – 2°K of T_N .

For only one of the three specimens analyzed (MnF_2) is the low-temperature fit impressive (Fig. 1). For CoF_2 , however, the theoretical and experimental curves parallel one another (Fig. 2) sufficiently closely so that we might hope for equally good agreement if a crystal of higher purity were used. At the same time, this could fail to hold true, because the Co^{++} ions may suffer transitions between low-lying levels and thus make their own contribution to the low-temperature resonance.¹⁷ Some evidence for this is found in the value of β which is nearly an order of magnitude greater than that for MnF_2 and which may be overestimated because of the neglect of the aforementioned transitions. In MnO, any theoretical fit at all requires a considerable stretch of imagination, and therefore further experiments on crystals of high purity are indicated.

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¹⁶ K. Kawasaki, Progr. Theoret. Phys. (Kyoto) **29**, 801 (1963).

¹⁷ G. A. Slack (private communication).