Application of the Inverted-Neutron-Filter Technique to the Study of Inelastic Scattering by Paramagnetic Substances*

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(Received 11 January 1966)

Using the filter-cutoff method we have measured the quasielastic scattering of slow neutrons from several paramagnetic compounds. Our results for MnF_2 at large scattering angles are in reasonable agreement with time-of-flight measurements by Cribier and Jacrot. For small scattering angles we have confirmed the Lorentz-like form of the energy distribution of scattered neutrons predicted by de Gennes. Similar measurements at large and small scattering angles on a partially inverted sample of $MnAl_2O_4$ did not exhibit the predicted angular dependence. This suggests that the assumption of A-A interactions only is inappropriate for this compound. From the temperature dependence of the intensity of the (200) magnetic reflection, a Néel temperature of 18°K was deduced for the $MnAl_2O_4$. Our results demonstrate that with an adequate flux of long-wavelength neutrons the inverted-filter technique can be employed successfully in studies of paramagnetic scattering.

I. INTRODUCTION

CURRENT theories of cooperative magnetic phenomena in nonmetals are based upon the well-known Heisenberg–Dirac–Van Vleck interaction,

$$V_{ij}=-2J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j, \tag{1}$$

between the ith and jth magnetic ions in a crystal. In this expression $\mathbf{S}_i$ and $\mathbf{S}_j$ are spin operators associated with the ith and jth ions, respectively, and J_{ij} is the familiar exchange interaction. Many years ago, Van Vleck[1,2] pointed out that in the high-temperature limit ($T\gg T_c$) this interaction gives rise to magnetic inelastic scattering of slow neutrons. More recently, de Gennes[3] and Sáenz[4] have treated the same problem using the time-dependent spin-correlation formulation introduced by Van Hove.[5] Subsequently, Jacrot and Cribier[6] compared de Gennes' results with neutron scattering data from MnF_2 using time-of-flight techniques. Because the half-width of the energy distribution decreases rapidly with decreasing scattering angles, they found it difficult to verify fully the predicted Lorentzian character of the line shape for small momentum transfer. Nevertheless, they established the plausibility of the Lorentzian line shape by observing that their experimental curve had wings whose magnitude was too large to be Gaussian in character.

The purpose of this paper is to demonstrate that the inverted-filter technique introduced by Brockhouse[7] and subsequently employed by Stiller and Danner,[8] and others[9,10] represents a simple and effective alternative method for investigating the quasielastic paramagnetic scattering described by the Van Vleck–de Gennes' theory. We will show that because of the high resolution attainable with this technique, the Lorentz-like behavior of the energy distribution for small momentum transfer can be verified easily.

II. THEORY

Using a method of moments and assuming nearest neighbor interactions only, Van Vleck[2] has shown that the root-mean-square energy change resulting from the magnetic elastic scattering process is given by the expression

$$(\Delta E)_{\mathrm{rms}}=2[\tfrac{2}{3}zS(S+1)]^{1/2}J. \tag{2}$$

In Eq. (2), z is the number of nearest neighbors, S the spin of the magnetic ion, and J is the exchange constant. It is clear, then, that a measurement of the energy distribution of neutrons scattered by a paramagnetic sample yields information about the magnetic-ion interaction.

De Gennes[3] subsequently combined the Van Vleck method of moments with the formalism introduced by Van Hove.[5] According to this formulation the statistical behavior of the spin assembly is represented in the magnetic neutron-scattering cross section by the function

$$p_\kappa(\omega)=\sum_R\int dt\,\exp[i(\boldsymbol{\kappa}\cdot\mathbf{R}-\omega t)]\times\langle\mathbf{S}_0(0)\cdot\mathbf{S}_R(t)\rangle[S(S+1)]^{-1}. \tag{3}$$

In the foregoing expression, $\hbar\kappa$ and $\hbar\omega$ are the momen-

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* Work performed under the auspices of the U. S. Atomic Energy Commission.
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[3] P. G. de Gennes, J. Phys. Chem. Solids **4**, 223 (1958).
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[7] B. N. Brockhouse, Bull. Am. Phys. Soc. **5**, 373 (1960).
[8] H. H. Stiller and H. R. Danner, in *Proceedings of the Symposium on Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 363.
[9] C. S. Choi, H. R. Danner, and A. N. Goland, Bull. Am. Phys. Soc. **9**, 297 (1964).
[10] E. A. Friedman and A. N. Goland, Bull. Am. Phys. Soc. **10**, 353 (1965).

tum and energy transfers, respectively, and

$$\langle \mathbf{S}_0(0)\cdot\mathbf{S}_R(t)\rangle[S(S+1)]^{-1}$$

is the time-dependent spin-correlation function. De Gennes derived approximate expressions for $p_\kappa(\omega)$ for the case of a polycrystalline sample in which only nearest neighbor interactions are important. If b is the nearest neighbor distance, then for $kb\gtrsim\pi$, he has shown that

$$p_\kappa(\omega)\approx\left[\frac{3\pi}{zS(S+1)}\right]^{1/2}\frac{\hbar}{2J}\exp\left[\frac{-3\hbar^2\omega^2}{16zS(S+1)J^2}\right], \quad (4)$$

whereas for $kb\rightarrow 0$,

$$p_\kappa(\omega)\approx\frac{2\Lambda_1\kappa^2}{\omega^2+(\Lambda_1\kappa^2)^2}. \quad (5)$$

These results are valid for those elements whose orbital magnetism is quenched so that the ions possess spin-only magnetic moments. From Eqs. 4 and 5 one observes that for large momentum transfers the energy distribution of the scattered neutrons is Gaussian whereas for small momentum transfers it becomes Lorentzian. In the transition from Gaussian to Lorentzian, the half-width decreases rapidly as a function of momentum transfer. For an insulator having eight nearest neighbors, the second moment of the Gaussian distribution is given approximately by the expression

$$\langle\hbar^2\omega^2\rangle\approx\tfrac{2}{3}[8S(S+1)(2J)^2], \quad (6a)$$

while the spin-diffusion coefficient Λ_1 becomes

$$\Lambda_1\approx 0.36b^2[S(S+1)]^{1/2}\frac{2J}{\hbar}. \quad (6b)$$

Using de Gennes' notation, one can write the complete magnetic differential scattering cross section for neutrons in the form

$$\frac{d^2\sigma}{d\Omega d\omega}=\text{const}\,\frac{k}{k_0}|F(\kappa)|^2 p_\kappa(\omega), \quad (7)$$

where k_0 and k are the scattering vectors of an incoming and outgoing neutron, respectively, and $F(\kappa)$ is the magnetic form factor.

III. EXPERIMENTAL METHOD

The experimental techniques employed in this work represent an improvement over those previously reported[8,11] A detailed description and comparison of our methods with those used before will appear in another publication.[12] The essential differences lie in our introduction of a BeO filter as part of the detection system as suggested by Brockhouse,[13] and in the insertion of a monitor before the sample. The availability of a higher flux of long-wavelength neutrons than that available to Stiller and Danner[8] also made it possible to determine the instrumental resolution by replacing the sample with a vanadium scatterer.

The inverted-filter method is an integral technique which does not analyze directly the energy distribution of the scattered neutrons. Instead, the energy E_0 of the neutrons incident on the sample is allowed to vary, and a filter interposed between the sample and the counter permits only those neutrons to be counted whose energy is less than the filter-cutoff energy E_f. For a monoenergetic incident beam the number of neutrons detected will be proportional to the product of the incident flux and the integral from zero to E_f over the energy distribution of the scattered neutrons, $S(E)$. In practice, there exists a distribution of incident energies arising from the finite resolution of the spectrometer, $R(E_0)$. Moreover, the number of neutrons detected depends upon the transmission $T(E)$ of the filter preceding the detector and upon the relative efficiency $\eta(E)$ of the monitor counter and the main counter. Thus, the quantity measured is

$$I(E_0)\propto\int_{-\infty}^{\infty}\int_0^{E_f}R(\epsilon-E_0)T(E)\eta(E)S(E-\epsilon)d\epsilon dE. \quad (8)$$

A schematic drawing of the experimental arrangement is shown in Fig. 1. A coarsely collimated beam of

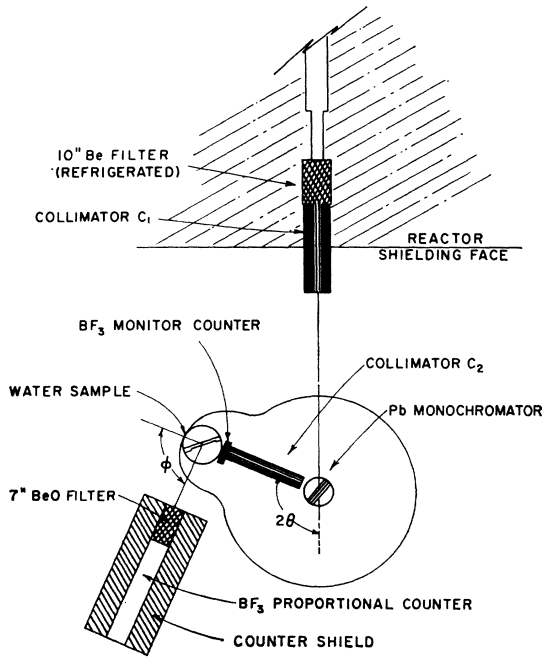

FIG. 1. Experimental arrangement for inverted-filter technique.

[11] H. Stiller and A. Hautecler, Z. Physik **166**, 393 (1962).
[12] C. S. Choi, H. R. Danner and A. N. Goland (unpublished).
[13] B. N. Brockhouse, in *Proceedings of the Symposium on Inelastic Scattering of Neutrons in Solids and Liquids, Vienna, 1960* (International Atomic Energy Agency, Vienna, 1961), p. 375.

neutrons emanating from the Brookhaven graphite reactor traverses 10 in. of polycrystalline beryllium refrigerated by liquid nitrogen before passing through a Soller collimator (C_1). The beam emerging from the collimator strikes a lead monochromating crystal oriented to reflect from a set of {111} planes. Those neutrons reflected by the monochromator in the direction 2θ with respect to the original direction of the beam, pass through a second collimator (C_2) and a monitor counter (M) before striking the sample. The angular positions of the sample (2θ) and the monochromator are coupled 2:1 so as to allow the energy of the neutron beam incident upon the sample to be continuously varied. Since the beryllium filter effectively transmits only those neutrons whose energies are ≤ 0.0052 eV ($\lambda \geq 3.96$ Å), incident energies greater than 5.2 meV are not available. The lowest incident energy attainable is approximately 2.85 meV, a limitation imposed by the angular range of the spectrometer ($2\theta_{\max} \sim 140°$).

Neutrons scattered by the sample in the direction φ with respect to the incident beam from the monochromator traverse a 7-in. polycrystalline BeO filter before reaching the BF_3 detector. This is the analyzing filter; it transmits only those neutrons whose energies are less than 3.74 meV.

The instrumental resolution can be determined in one of two ways: The detector can be set at zero degrees ($\varphi=0$) and the incident energy varied through a region around the BeO cutoff energy. Alternatively, a vanadium sample can be inserted and the detector set at an arbitrary scattering angle, φ. Variation of the incident neutron energy around the BeO cutoff can be performed again. The first method measures directly the transmission of the BeO and from the shape of the cutoff one can derive the energy resolution of the instrument. Since vanadium is an incoherent scatterer, the second method should yield the same shape for the filter cutoff independently of the choice of φ. Figures 2 and 3 are representative of each type of measurement. Figure 2 shows the BeO cutoff measured indirectly with vanadium at a scattering angle of 60°, and directly for $\varphi=0$ without vanadium. For the collimation employed, the energy resolution was found to be 1%. Analogous results for different collimation and a scattering angle of 90° are shown in Fig. 3. In this case the energy resolution turned out to be 2.5%. The latter collimation was employed throughout the measurements reported here because of the higher counting rates it afforded, and because the expected broadening did not necessitate the higher resolution. Because of the low neutron flux, collimation after the sample could not be employed. Consequently, some uncertainty in the scattering angle had to be tolerated.

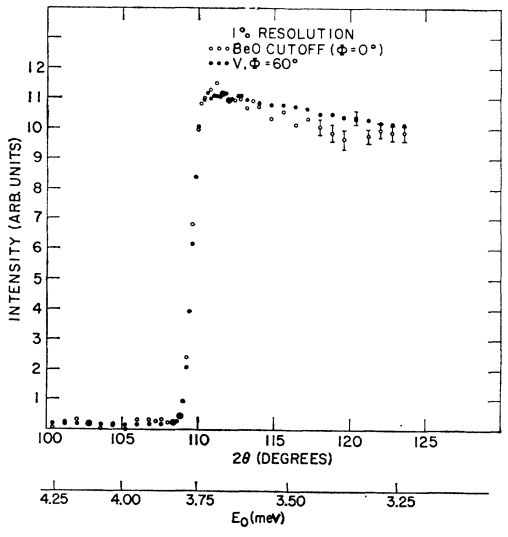

FIG. 2. Comparison of transmitted intensity of the BeO cutoff measured indirectly with vanadium sample for $\varphi=60°$ and directly with no sample for $\varphi=0°$. Resolution is 1 %.

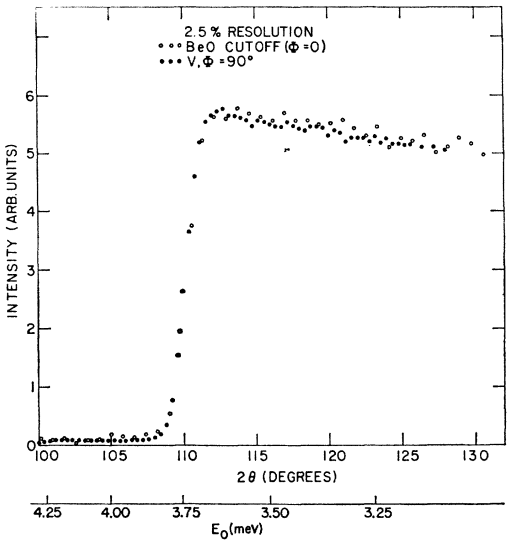

FIG. 3. Comparison of transmitted intensity at the BeO cutoff measured indirectly with vanadium sample for $\varphi=90°$ and directly with no sample for $\varphi=0°$. Resolution is 2.5 %.

IV. METHOD OF DATA ANALYSIS

Since the inverted-filter technique is not widely used, a brief description of our method of data analysis is warranted. Equation (8) shows that the quantity measured is proportional to an integral over the energy distribution of the scattered neutrons, $S(E-\epsilon)$. This distribution, given by Eq. (7), is the differential scattering cross section, and in addition to the function $p_\kappa(\omega)$ it contains the square of the magnetic form factor, $|F(\kappa)|^2$. The most convenient way to incorporate the latter quantity in a computer program to perform the integration represented by Eq. (8) is to approximate $F(\kappa)$ by an analytic function. We have been able to obtain a good fit to existing data[14] for Mn^{2+} by assuming

[14] J. N. Hastings, N. Elliot, and L. M. Corliss, Phys. Rev. 115, 16 (1959).

that $F(\kappa)$ has the functional form of a Padé approximant in even powers of κ up to the fourth power, that is, by letting

$$F(\kappa)=\frac{1+a_1\kappa^2+a_2\kappa^4}{1+b_1\kappa^2+b_2\kappa^4}. \quad (9)$$

The approximation becomes poor for values of κ greater than 4. However, contributions to the integral from beyond this value of the momentum transfer are small so that errors in the value of $|F(\kappa)|^2$ are not important.

It must be pointed out also that κ does not remain constant during the experiment. Instead, the scattering angle φ is fixed while E_0 varies. This means that κ must be replaced in the integrand by its equivalent: $(k_0^2+k_1^2-2k_0k_1\cos\varphi)^{1/2}$. Since the neutron energy E is related to k, the preceding expression can be rewritten as a function of E, E_0, and φ. Similarly, the factor k/k_0 which appears in the cross section can be rewritten as $(E/E_0)^{1/2}$.

The numerical integration of Eq. (8) was performed on an IBM 7094 computer. For large momentum transfers where $p_\kappa(\omega)$ is Gaussian the full width at half-maximum was treated as a parameter. For small momentum transfers the only parameter was Λ_1, the spin diffusion constant defined by Eq. (5).

The form of each of the remaining energy-dependent functions, the instrumental resolution, the BeO-filter transmission and the relative efficiency of the monitor and detector counters, was determined experimentally and included in the computer program.

V. RESULTS

A. MnF_2

MnF_2 is a well-understood compound whose Néel temperature is 72°K. Its magnetic properties can be explained on the basis of nearest neighbor interactions

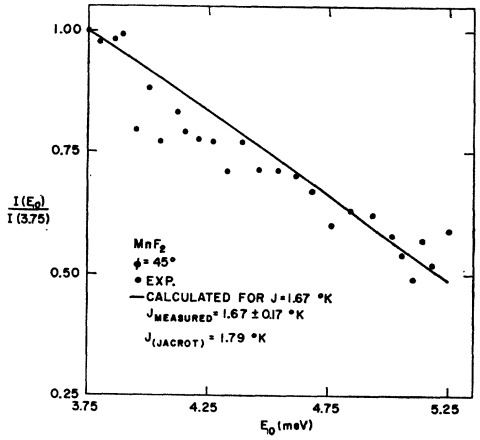

FIG. 4. Results of measurements on MnF_2 powder sample for a scattering angle of 45°. The solid line represents a Gaussian energy distribution.

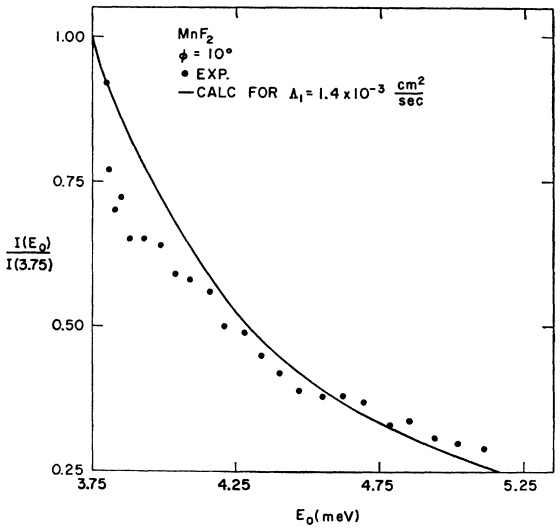

FIG. 5. Results of measurements on MnF_2 powder sample for a scattering angle of 10°. The solid curve represents a Lorentzian energy distribution.

alone. Moreover, it is readily obtainable in the form of an anhydrous powder. Thus, it represents an ideal material to study by means of a new technique. Neutron-scattering data taken at room temperature should be consistent with the de Gennes theory quoted in Sec. II.

The room-temperature results for a scattering angle of 45° are shown in Fig. 4. The data were normalized to the intensity at the BeO cutoff, after correcting for the contribution from nuclear incoherent elastic scattering at this energy. The normalized intensities were plotted as a function of incident neutron energy. The magnitude of κb is greater than π for all incident-energies at this scattering angle. Therefore, in accordance with Eq. (4) the solid line in the figure was calculated by integration of Eq. (8) using a Gaussian to represent the energy distribution of scattered neutrons. The root-mean-square energy represented by this Gaussian corresponds to a J value of 1.67°K. The scatter in the data reflects the very low counting rates, and the signal-to-noise ratio of only 2 to 1. Our ability to fit these data has an estimated error of $\pm 10\%$ under these conditions. The corresponding J value deduced by Cribier and Jacrot with an estimated precision of 1% is 1.79°K.

In order to investigate the predicted Lorentz-like behavior of the energy distribution, we have measured the scattering from the sample at an angle of 10°. This corresponds to a κb value of about 0.88. The experimental results shown in Fig. 5 are clearly indicative of a Lorentz-like energy distribution with its characteristically long tail. These data cannot be represented by any Gaussian distribution. The solid curve shown in the figure has been calculated by the method outlined in Sec. IV using a value for the spin-diffusion constant, Λ_1, of 1.4×10^{-3} cm²/sec. From Eq. (6b) and the value

of 1.67°K for J deduced from the 45° scattering data, one obtains a Λ_1 value of 0.68×10^{-3} cm^2/sec. The agreement is reasonably good since MnF_2 does not possess the simple-cubic magnetic symmetry required by de Gennes's theory. Moreover, experimentally the acceptance angle for the scattered radiation had a width of several degrees so that we were measuring an average over scattering angles and, therefore, over momentum transfers.

B. $MnAl_2O_4$

Our results for MnF_2 demonstrate the feasibility of measuring an exchange constant of the order of a few tenths of a degree Kelvin. J values of this magnitude will produce a broadening which is large compared to the resolution of the spectrometer. However, the low flux available to us placed serious limitations upon the selection of a suitable magnetic compound expected to have a J value in this range. Our attention ultimately fixed upon the spinel, $MnAl_2O_4$, whose magnetic properties have been reported by Roth.[15] In this compound manganese ions in the plus-2 state occupy principally the spinel A sites while the paramagnetic aluminum ions reside upon the B sites. Thus the dominant magnetic interaction was expected by Roth to be the A-A interaction between neighboring Mn^{2+} ions. Since his magnetic susceptibility data failed to show a maximum which could be identified with the magnetic ordering temperature, Roth estimated the latter parameter from the degree of saturation of the magnetic moment at 4.2°K as deduced from neutron-diffraction data. He concluded that T_c is 6.4°K although he suggested that it might be somewhat higher since χ^{-1} begins to show deviations from the Curie-Weiss law at about 20°K. Finally, Roth deduced from molecular-field theory that for T_c equal to 6.4°K and four nearest-neighbor Mn^{2+} ions, $J\approx0.3$°K. Fortunately, we were able to obtain our data from the same powder employed by Roth in his experiments. Although the statistics were very poor again, two conclusions could be drawn from these data (Fig. 6).

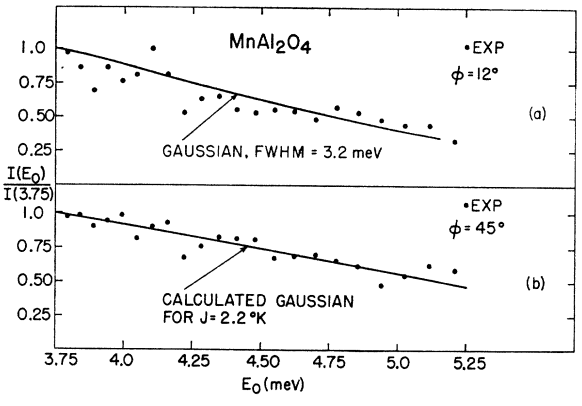

FIG. 6. (a) Results for $MnAl_2O_4$ powder for scattering angle of 12°. The solid curve represents a Gaussian energy distribution. (b) Results for $MnAl_2O_4$ powder for scattering angle of 45°. The solid curve represents a Gaussian energy distribution.

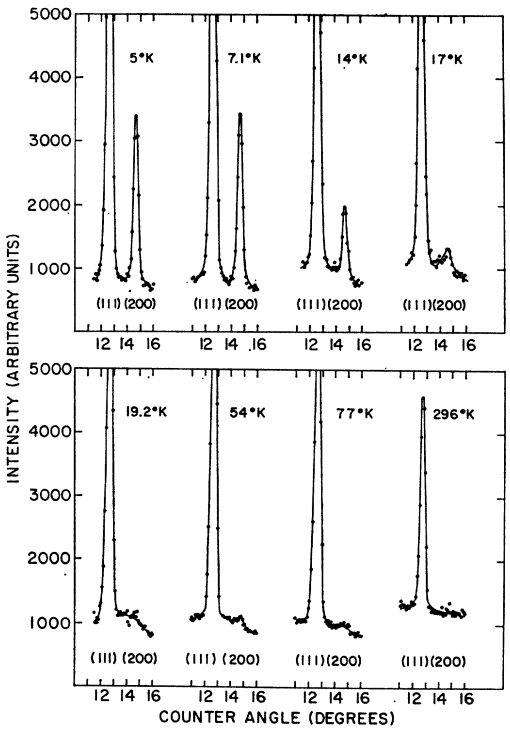

FIG. 7. Intensity of (111) and (200) reflections from $MnAl_2O_4$ powder sample as a function of temperature. The (200) reflection is a purely magnetic superlattice line.

First, both the small-angle scattering from this material and the large-angle data could be fitted with a Gaussian distribution. The absence of Lorentz-like behavior for small momentum transfer might be explained by the presence of short-range order or it might be due to the existence of interactions between ions other than nearest neighbors. The latter possibility is consistent with the fact that θ and T_N are quite different in magnitude. In addition, Roth has estimated from his neutron-diffraction data that the degree of inversion for this sample is about 4%. Thus, 4% of the manganese ions reside on B sites. If the A-B interaction were very strong compared to the A-A interaction, an inversion of only 4% might be sufficient to explain our results. Moreover, Roth[16] has detected a small ferrimagnetic component in his susceptibility data; this further invalidates the originally simple assumption of A-A interactions only.

Second, if one uses the 45° data to determine the magnitude of the exchange interaction from an equation analogous to (6a) but with four nearest neighbors

[15] W. L. Roth, J. Phys. Radium 25, 507 (1964).

[16] W. L. Roth (private communication).

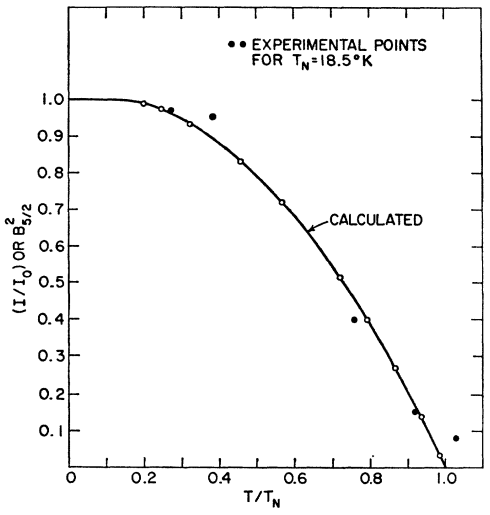

FIG. 8. A comparison of the temperature dependence of the integrated intensity of the (200) reflection with the square of the Brillouin function corresponding to $S=\frac{5}{2}$.

instead of eight, he finds that J is ~ 2.2°K. This is to be compared with Roth's estimate of ~ 0.3°K.

The foregoing observations suggested that a more accurate determination of the Néel temperature was needed. Therefore, we have measured the intensity of the (200) magnetic reflection as a function of temperature. The results are shown in Fig. 7. As expected, the data show evidence of short-range order at temperatures well-above the Néel temperature. This can be seen clearly in the data taken at liquid-nitrogen temperature. That the residual intensity was indeed short-range order and not second-order contamination was verified by the insertion into the beam of a plutonium filter having a strong resonance at half the primary wavelength of 1.05 Å. Assuming that the temperature dependence of the magnetic moment can be described by the Brillouin function corresponding to $S=\frac{5}{2}$, one can estimate the Néel temperature from these data. The intensity of the (200) peak should be proportional to $(B_{5/2})^2$ and should go to zero at T_N. Figure 8 represents this behavior for our data; we have normalized the intensity to the value estimated for 0°K. A reasonable fit is obtained for a Néel temperature of about 18°K. It will be recalled that the temperature variation of χ^{-1} reported by Roth suggested a value around 20°K.

VI. CONCLUDING REMARKS

The preceding results indicate that the inverted-filter technique represents a simple experimental method for determining the exchange interaction of a magnetic compound in its paramagnetic state. The only experimental limitation arises from the difficulty in obtaining a high flux of cold neutrons. This problem has been overcome at some reactors through the introduction of cold moderators or curved beam pipes. Where these techniques are employed, the inverted-filter method should be given serious consideration as a means of investigating any quasielastic scattering process. With regard to the application reported in this paper, it is clear that further theoretical work is required in order to extend the results beyond nearest-neighbor interactions and to cover crystal symmetries other than that of the simple-cubic lattice. Unfortunately, explicit theoretical expressions other than those of de Gennes also have been confined to this simple case.[4,17,18]

ACKNOWLEDGMENTS

We would like to express our gratitude to J. Milazzo for performing the computer calculations, and to various members of the Solid-State Group at Brookhaven for helpful discussions. We also wish to thank Dr. W. L. Roth for allowing us to use a sample of $MnAl_2O_4$ taken from the powder which he prepared, and for discussing the magnetic properties of this material.

[17] H. Mori and K. Kawasaki, Progr. Theoret. Phys. (Kyoto) 27, 529 (1962).

[18] H. S. Bennett and P. C. Martin, Phys. Rev. 138, A608 (1965).