Magnetic short-range order in Gd

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The magnetic short-range order in a ferromagnetic, isotopically enriched ^{160}Gd metal single crystal has been investigated by quasielastic scattering of 81-meV neutrons. Since Gd behaves as an S-state ion in the metal, little anisotropy is expected in its magnetic behavior. However, the data show that there is anisotropic short-range order present over a large temperature interval both above and below T_C. The data have been analyzed in terms of an Ornstein-Zernike Lorentzian form with anisotropic correlation ranges. These correlation ranges as deduced from the observed data behave normally above T_C but seem to remain constant over a fairly large interval below T_C before becoming unobservable at lower temperatures. These observations suggest that the magnetic ordering in Gd may be a more complicated phenomenon than first believed.

I. INTRODUCTION

Gadolinium metal was shown to be ferromagnetic below $T_C \cong 291.0$ K by magnetization[1] and specific-heat[2] measurements many years ago. This rare-earth metal should exhibit little anisotropy since its $4f^7$ configuration is spherically symmetric and can be well described by $4f^7$ Gd^{3+} ions imbedded in a conduction-electron sea. In single-crystal magnetization[1] measurements, however, some anisotropy is observed at temperatures below T_C.

Gadolinium is not a good sample to study by neutron scattering since natural Gd has one of the highest thermal-neutron absorption cross sections of any element. However, by using epithermal neutrons, Cable and Wollan[3] were able to show that no spiral structure exists. Their experiments have shown that Gd is a simple ferromagnet whose moment direction varies with temperature. The magnetic-moment direction is parallel to the c axis at T_C and departs from this direction at $T_0 \simeq 232$ K. The angle ϕ between $\vec{\mu}$ and the c axis departs from zero abruptly at T_0, then goes through a broad maximum, reaches $\phi = 65°$ at $T = 183$ K, and then decreases to about 32° at $T = 10$ K.

Low-field-magnetization,[1] specific-heat,[2] and other[4] data show anomalies at T_0 which led early authors[5] to believe that Gd had a spiral structure for $T_0 < T < T_C$ and became ferromagnetic at T_0. Although this interpretation was shown to be incorrect by the neutron-scattering results, an explanation of this anomalous behavior is still lacking.

Recently, an isotopically enriched sample of Gd was produced by the Isotopes Division of the Oak Ridge National Laboratory (ORNL) and single crystals were grown from this material by the strain-anneal method. A large single-crystal grain of this 99.99% ^{160}Gd was used to observe the spin-wave dispersion of the ferromagnetic state of Gd (see Ref. 6) at low temperatures to determine the spin-spin interaction parameters. Small crystals of the same material were used to measure very accurately the form factor of the magnetic electrons in Gd,[7] which could be compared to theoretical calculations of the electron wave functions.

The present paper[8] presents the results of a study of the quasielastic neutron scattering of high-energy neutrons from the same large grain which was used for the spin-wave results. These experiments were undertaken with two main purposes in mind: first, to investigate the anomaly mentioned above which occurs near T_0, and second, as a preliminary investigation of the critical behavior of this ferromagnet.

II. EXPERIMENT

The initial step in the investigation of magnetic diffuse scattering from Gd, which will be discussed in this paper, used neutrons of 1-Å wavelength which have a sufficiently high incident energy (81 meV) that it is a good approximation to neglect energy changes in the scattering. With this approximation, one obtains an overall description of the static spin-spin correlation function. The dynamic properties of Gd will be reported in the future using inelastic neutron-scattering techniques. A completed portion of that work shows that, at least above ~150 K, the quasielastic approximation is quite good since the excitation energies are small.

We use the formula given by Marshall and Lovesey[9]

$$\frac{d^2\sigma}{d\Omega\, d\omega} = \mathrm{const} f^2(q) k_B T \frac{\hbar\omega/k_B T}{e^{\hbar\omega/k_B T} - 1} \frac{k_F}{k_I} \times \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta) S^{\alpha\beta}(\vec{q}, \omega), \quad (1)$$

where $(\hbar\omega/k_BT)/(e^{\hbar\omega/k_BT}-1)$ is the detailed balance factor, k_I and k_F are the initial and final wave vectors of the neutron, $S^{\alpha\beta}(\vec{q},\omega)=\chi^{\alpha\beta}(\vec{q})F^{\alpha\beta}(\vec{q},\omega)$ is the Fourier transform of the correlation function $\langle S_0^\alpha(0)S_R^\beta(t)\rangle$ over time and space, and α, β represent, x, y, or z coordinates with $\hat{Q}_\alpha$ the αth component of a unit vector along $\vec{Q}=\vec{k}_F-\vec{k}_I$.

If the characteristic energy changes $\hbar\omega$ of the neutrons scattered by the sample are small compared to the initial energy of the neutron and small compared to the resolution of the neutron spectrometer, the quasielastic approximation[9] is a valid measurement of the generalized q-dependent susceptibility $\chi(\vec{q})$ of the sample. This is because a constant scattering angle scan will effectively integrate the true energy-dependent scattering over energy at constant $\vec{q}$. Since the energy-dependent factor in the function $S(\vec{q},\omega)$ which describes the response of the scattering system to the neutron probe is defined to be normalized so that the integral over ω is unity at constant $\vec{q}$, the counter effectively performs this integration automatically and removes the factor $F(\vec{q},\omega)$ from S. Inelastic experiments on Gd show that although the maximum spin-wave energy at 78 K is about 24 meV,[6] the excitation energies for $T>150$ K are small and very small indeed above 250 K, typically from 0.1 to 1 meV. Since the incident neutron energy was 81 meV, we assume throughout this paper that the constant scattering angle scans do integrate over energy sufficiently accurately to make the use of the quasielastic approximation valid for these data and hence the observed intensity is proportional to $\chi(\vec{q})$.

The crystal was mounted in a cryostat with the $\vec{b}_1$, $\vec{b}_3$ reciprocal-lattice vectors in the scattering plane and the intensity was measured as a function of $\vec{q}=\vec{Q}-\vec{\tau}$, where $\vec{\tau}$ is one of the reciprocal-lattice vectors from the origin to (1, 0, 0), (1, 0, 1) or (0, 0, 2) Bragg points in this plane. In addition, some data were collected in the (hhl) plane near (1, 1, 0) and (0, 0, 2) which data showed the same qualitative behavior as the $(h0l)$ plane results.

In a single-domain ferromagnet, the sum over α and β in Eq. (1) gives

$$(1+\hat{Q}_\parallel^2)S_\perp(\vec{q},\omega)+(1-\hat{Q}_\parallel^2)S_\parallel(\vec{q},\omega)\,, \tag{2a}$$

which becomes

$$(1+\hat{Q}_\parallel^2)\chi_\perp(\vec{q})+(1-\hat{Q}_\parallel^2)\chi_\parallel(q) \tag{2b}$$

in the quasielastic approximation. As long as the ordered moment is parallel to the unique c direction of the hexagonal lattice, Gd consists of plus and minus magnetic domains which are equivalent in Eq. (2b) so that this formula applies for $T_0<T<T_C$. Thus, if we measure near (0, 0, 2) $\hat{Q}_\parallel^2=1$, and only $\chi_\perp(\vec{q})$ will be observed; near (1, 0, 0), $\hat{Q}_\parallel^2=0$ and $\chi_\perp(\vec{q})+\chi_\parallel(q)$ will be present. Both $\chi_\perp$ and $\chi_\parallel$ are believed to have the Ornstein-Zernike form (perhaps modified as discussed by Fisher[10]) in which they are described at small $|q|$ by Lorentzian functions of $|q|$ with inverse range parameters $\kappa_\perp$ and $\kappa_\parallel$.

Figure 1 shows typical scans at different temperatures. The midpoints of the scans are located at approximately the same magnitude of $|\vec{q}|$ away from the (1, 0, 0) and (0, 0, 2) reciprocal-lattice points. These data show that the scattering away from the Bragg peaks (the width of the Bragg peak is of order 0.002 ξ units) is still appreciably $\vec{q}$ dependent at these temperatures, and that the intensity around (0, 0, 2) differs markedly from that around (1, 0, 0). The width in q_x of the scattering at (0, 0, 1.8) indicates that a great deal of short-range order is present in the crystal and the fact that the scattering at (0.9, 0, 0) shows no such peak (the magnitudes of $\vec{q}$ are nearly equal) shows that this short-range order is predominantly within the basal planes of the hcp structure. Thus a ferromagnetic short-range order in the basal planes results in ridges of scattering intensity parallel to $\vec{b}_3$ in reciprocal space peaked around each allowed reciprocal lattice point. The solid curves are least-squares fits of the data to Lorentzian functions of q_x, the parameters of which are the Lorentzian peak height, peak width, peak position, and two parameters to describe a linear background under the peak. These fits describe the data remarkably well even though such a form for the scattering is only valid for small q theoretically. Furthermore, for the scans perpendicular to the $00l$ direction, such a fitting function works well for all temperatures from 80 to 420 K and for $-0.5b_1\le|\vec{q}_x|\le+0.5b_1$ with only the peak height and width changing with T.

Figure 2 depicts the temperature dependence of the peak intensity for scans whose midpoints are at values of $\vec{q}$ near (0, 0, 2). Above $T_C=291$ K, the decrease of intensity is typical of short-range order above a magnetic transition, but, usually, this same behavior would be observed below T_C. Here, however, the intensity does not decrease as rapidly until $T_0=232$ K is reached. Therefore, the short-range order in the basal planes is relatively insensitive to temperature in this region, and only decreases appreciably below T_0 as the magnetic ordering becomes more complete.

Figure 3 shows the least-squares fitted values of the width in q of the short-range-order peak versus T and illustrates that the correlation range of the short-range order remains relatively constant over a wide temperature region. Above T_C, the width increases as the correlation range decreases as would be expected, and below T_0, the

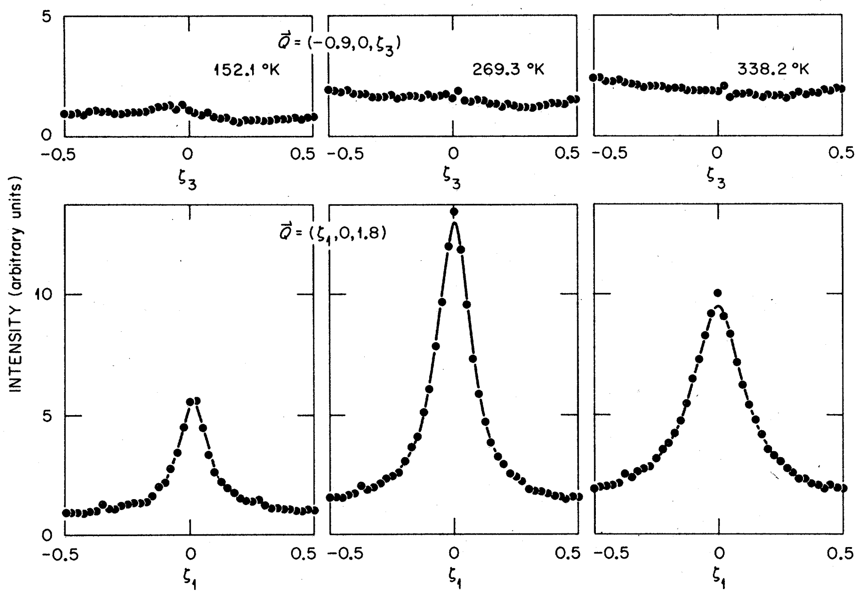

FIG. 1. Neutron short-range-order intensity vs Q near (1,0,0) and (0,0,2) Bragg peaks at three temperatures. $\vec{q} = \vec{Q} - \vec{\tau}$ is approximately equal in magnitude at the midpoints of the two $\vec{Q}$'s used. The Lorentzian fits are shown by solid lines for the (0,0,2) scans.

width decreases as the magnetic order becomes saturated.

For scans in the basal plane near (1, 0, 0) or (1, 1, 0), the intensity should be the sum of two Lorentzian peaks because $\chi_\perp + \chi_\parallel$ is measured here. Quantitative comparison of the intensities near these Bragg peaks with that measured around (0, 0, 2) is not possible due to the different absorption of this asymmetric, crescent-shaped crystal in the two orientations. In addition, the high extinction present in the Bragg peaks precludes using their intensities for internal normalization.

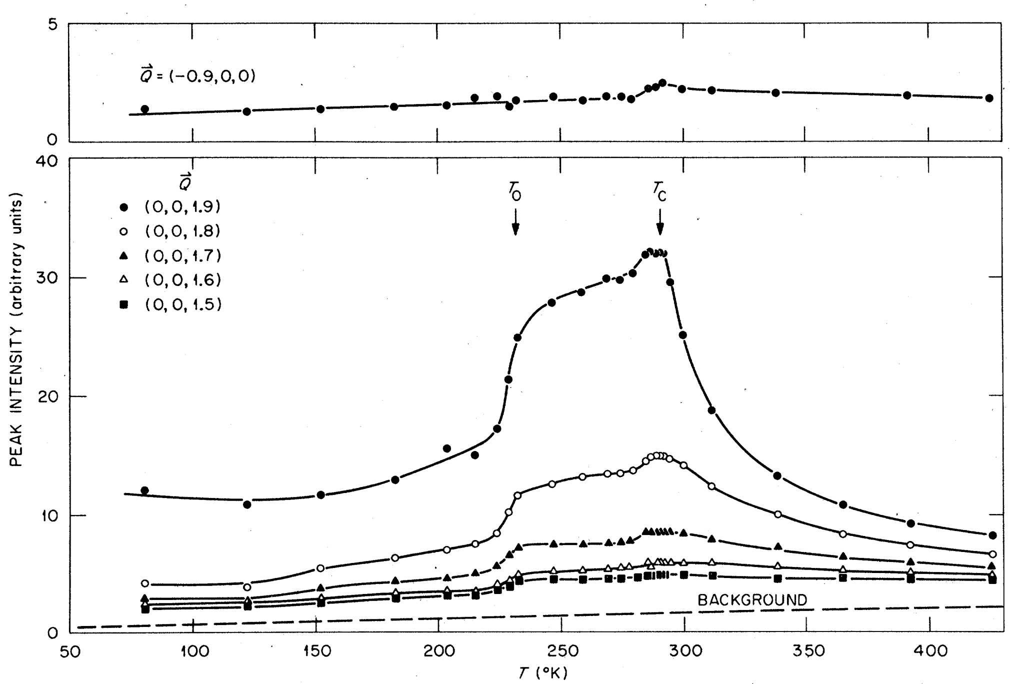

FIG. 2. Temperature dependence of the least-squares-fitted peak intensities for the scans near (0, 0, 2) compared to the observed intensity at $\vec{Q} = (-0.9, 0, 0)$ away from the 100 which is not the result of fitting. The magnitudes of $|\vec{q}|$ are approximately equal for (0, 0, 1.8) and (−0.9, 0, 0). The curves are only guides for the eye.

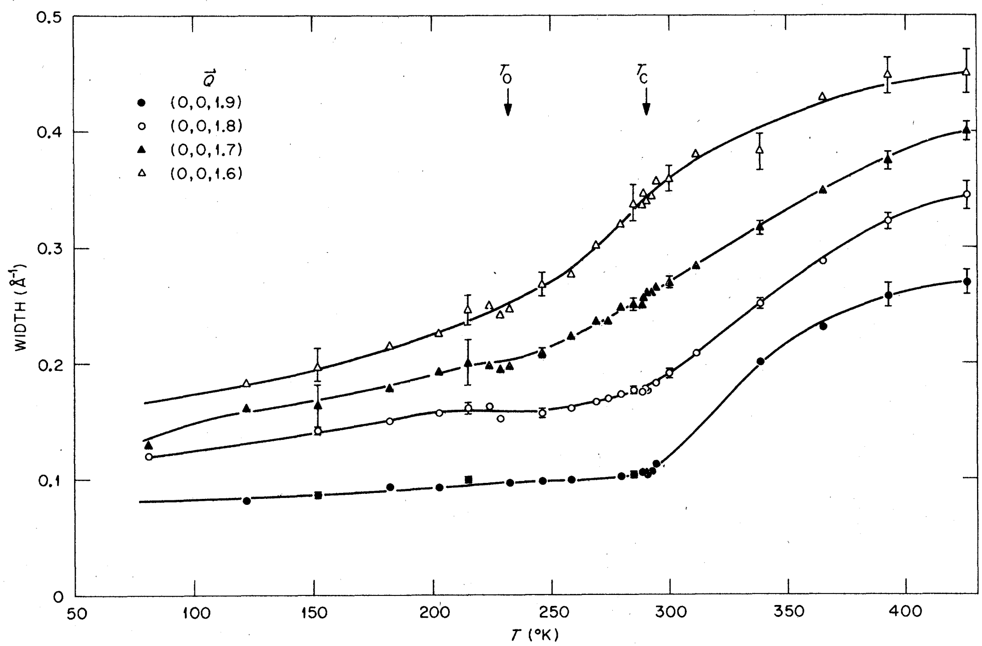

FIG. 3. Temperature dependence of the fitted Lorentzian widths for scans near the (0, 0, 2) perpendicular to the [00l] line in reciprocal space.

Least-squares fitting of the data to the sum of two Lorentzians for the basal plane runs was unsuccessful because no evidence for more than one peak is present in these data. Diffuse peaks are visible only at much smaller q values away from the base plane reciprocal lattice points as shown by the data in Fig. 1 and at the small q needed to observe the diffuse peak, a contamination from the tail of the large nearby Bragg peak was possible in the smallest q runs. These complications presented serious difficulties, but since a single peak appeared to describe the data well, these runs in the basal plane were also least-squares fitted to a single Lorentzian form.

Within these restrictions, the results of fitting data in the base plane to single Lorentzian peaks has yielded some information. Figures 4 and 5 show least-squares peak heights and peak widths versus temperature for scans parallel and perpendicular, respectively, to the [100] direction whose midpoints are located at the $\vec{Q}$'s shown. The data in Fig. 4 seem to qualitatively agree

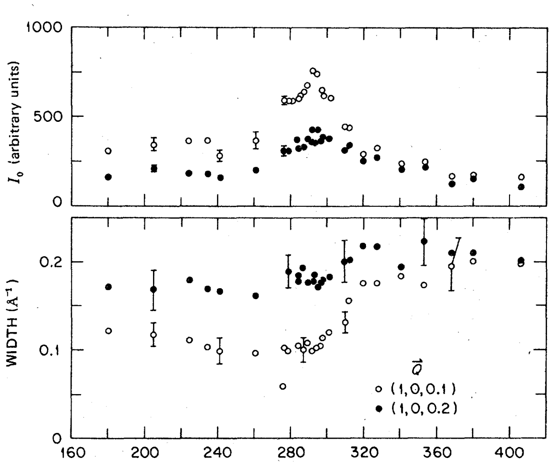

FIG. 4. Temperature dependence of the fitted Lorentzian peak heights and peak widths for scans near 100 perpendicular to the [00l] line.

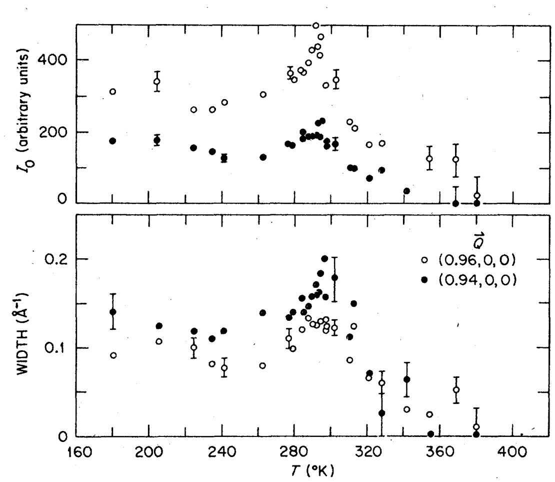

Fig. 5. Temperature dependence of the fitted Lorentzian peak heights and peak widths for scans near 100 perpendicular to the [h00] line.

(within a scale factor for peak height) with the corresponding data for the [00l] runs shown in Figs. 2 and 3 although there does not seem to be the pronounced drop in peak height at T_0 for the data near (1, 0, 0) that there is in Fig. 2. The data in Fig. 5 show a remarkable drop in width above T_C which simply does not exist in the corresponding type of scans near (0, 0, 2) which are shown in Fig. 6 where the peak heights and widths are plotted vs temperature for scans in which $\vec{q}$ varied parallel to the [00l] line at the same constant q_x values away from (0, 0, 2). This behavior is completely unexpected theoretically as far as the author has been able to ascertain and an explanation is presently unknown.

III. DISCUSSION

It is obvious from these results that a large amount of ferromagnetic short-range order exists in Gd throughout a wide temperature region above and below T_C. The diffuse peaks due to this scattering can be described by ellipses of equal intensity around each Bragg spot with the major axis of the ellipse parallel to $\vec{b}_3$ in reciprocal space. Thus, an anisotropic correlation between spins must be present which is long range and, due to this long range, is most conveniently described by an Ornstein-Zernlike Lorentzian form as opposed to a Fourier series in the correlation coefficients[11] which would require a prohibitively large number of terms. Equation (13.29) of Marshall and Lovesey[9] gives

$$\frac{\chi(\vec{q})}{\chi_0}=\frac{1}{(|T-T_C|)/T_C+[1-J(\vec{q})/J(0)]} \tag{3}$$

for the susceptibility function near T_C of a ferromagnet in which $J(\vec{q})$ is the Fourier transform of the exchange integral $J(\vec{R})$ and χ_0 is the noninteracting susceptibility. $J(0)$ is a maximum of $J(\vec{q})$ since Gd is ferromagnetic. If one expands $J(\vec{q}) = J(0) - (D_x q_x^2 + D_y q_y^2 + D_z q_z^2)$, one obtains an anisotropic Ornstein-Zernlike form for the neutron scattering

$$I(q)=\frac{I_0}{1+q_x^2/\kappa_x^2+q_y^2/\kappa_y^2+q_z^2/\kappa_z^2}, \tag{4}$$

where I_0 is a temperature-dependent constant and the κ's are inverse correlation ranges. This derivation is only valid for small $|q|$ but the present data show that this form for the intensity is a reasonably correct representation all the way to the zone boundaries perpendicular to the [00l] direction. The acoustic-spin-wave dispersion[6] is anisotropic in Gd, so, since κ^2 is inversely proportional to the spin-wave stiffness constant D, the anisotropic Lorentzian form is not unexpected.

Thus, in general, three different widths may be observed for each of $\chi_\perp$ and $\chi_\parallel$ for a total of six inverse correlation parameters ($\chi_\perp$ and $\chi_\parallel$ are expected to have different ranges from molecular-field theory).[9] Restricting our attention to the ($h0l$) plane, we have $\kappa_\perp^x$, $\kappa_\perp^z$, $\kappa_\parallel^x$, and $\kappa_\parallel^z$ where the superscript will be used to designate x, z parallel to [100] and [001] directions, respectively. We will reserve κ for the inverse correlation parameters and use W for the effective width of any particular type of scan. Around (002) reflection above T_0 the observed widths W as determined by least squares are given by

$$W_\perp^2(l)=\kappa_\perp^{x2}(1+q_l^2/\kappa_\perp^{z2}).$$

and

$$W_\perp^2(h)=\kappa_\perp^{x2}(1+q_h^2/\kappa_\perp^{x2}),$$

with similar expressions for $\chi_\parallel$ around a (100) reflection. From these expressions, $\kappa_\perp^x$ and $\kappa_\perp^z$ can be obtained from the least-squares values of the widths $W(l)$ and $W(h)$ for scans at different q_l and q_h away from the (002) by plotting W^2 vs q^2 and extrapolating to $q^2=0$. These results are shown in Fig. 7 for those temperatures where plots of this type were linear. Neither $\kappa_\perp^x$ nor $\kappa_\perp^z$ are zero below T_C but instead seem to be constant. This observation indicates some remanent disorder persists even in the ordered ferromagnetic phase of Gd.

It was not possible to determine $\chi_\parallel^{x,z}$ from the present data since apparently these parameters are so small that they are negligible compared to $\chi_\perp^{x,z}$ at the q values which we can use. Further experiments with considerably better q resolution might make it feasible to determine these parameters. However, such experiments would prob-

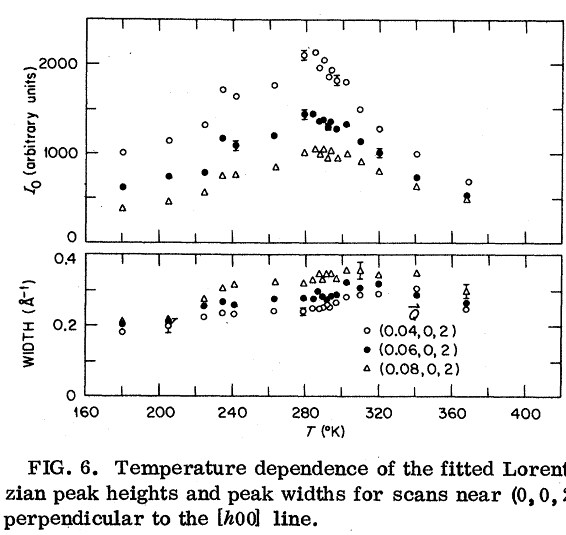

FIG. 6. Temperature dependence of the fitted Lorentzian peak heights and peak widths for scans near (0, 0, 2) perpendicular to the [h00] line.

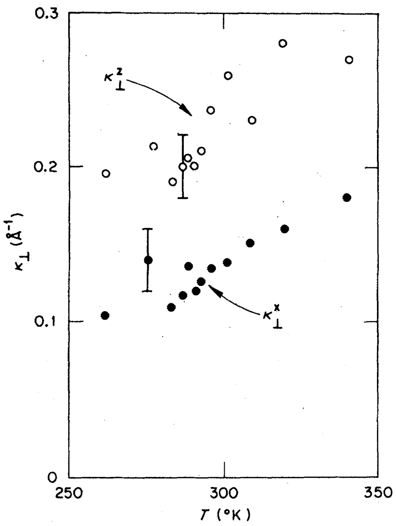

FIG. 7. Temperature dependence of $K_\perp^z$ and $K_\perp^x$ measured as described in the text near (0, 0, 2).

ably violate the quasielastic approximation since the only practical method of obtaining significantly better q resolution is to use a lower incident neutron energy. These important parameters may be obtained from the planned inelastic scattering experiments.

IV. SUMMARY

The present experiments have shown that the magnetic order in Gd is more complicated than would at first seem likely. Perhaps a more realistic theoretical picture of short-range order could resolve some of the questions raised by these results. The main results are: (i) magnetic short-range order in Gd is anisotropic, reflecting the long-range character of the magnetic interactions and the uniaxial nature of the hcp structure; (ii) some magnetic disorder persists well below T_C perhaps reflecting the disordered components of the magnetic moment vector when visualized classically; and (iii) the unexpected and surprising drop in width of the short-range-order peak near 100 above T_C which is, so far, unexplained. Further study of the short-range order in Gd is planned by inelastic-neutron experiments.

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