PHYSICAL REVIEW VOLUME 180, NUMBER 2 10 APRIL 1969

Paramagnetic Spin Waves and Correlation Functions in NiF_2

PAUL A. FLEURY
Bell Telephone Laboratories, Holmdel, New Jersey

(Received 30 September 1968)

The temperature dependence of one- and two-magnon excitations in NiF_2 has been studied by the technique of inelastic light scattering. Above the Néel temperature of 73°K, the one-magnon scattering disappears in accordance with the vanishing of long-range magnetic order. The two-magnon peak persists and remains underdamped in the paramagnetic phase at least to a temperature of $1.5T_N$. Some paramagnetic scattering is evident even at $4T_N$. Since the two-magnon excitations observed consist of pairs of very-short-wavelength spin waves, these observations confirm the existence of underdamped spin waves well into the paramagnetic phase. It is emphasized that the two-magnon scattering of light is sensitive to a four-spin correlation function, in contrast to the two-spin correlation function which determines neutron scattering from individual spin waves of comparably short wavelength. These experiments constitute the first measurement of a four-spin correlation function in the paramagnetic phase.

IN this paper, we report the observation of magnetic light scattering in NiF_2 in both its antiferromagnetic and paramagnetic phases. The most striking feature of these observations is the continuous evolution of the two-magnon scattering as the temperature is raised from well below to well above the Néel temperature, indicating the persistence of short-wavelength spin waves well into the paramagnetic phase. The spectrum of light scattered from NiF_2 was observed between 1.8 and 300°K. The Néel temperature T_N is 73°K. As expected from the disappearance of long-range magnetic order at T_N, the one-magnon peak vanishes for $T>T_N$. The two-magnon peak, however, persists and remains well defined to temperatures of at least $1.5T_N$, indicating the existence of underdamped spin waves in the paramagnetic phase.

We present below the detailed behavior of the frequency, linewidth, and integrated intensity of the two-magnon scattering as the system evolves from its antiferromagnetic to its paramagnetic phase. We shall also note the complementary nature of experiments which study short-wavelength excitations in first order (e.g., neutron scattering) as opposed to second order (light scattering) in hopes of motivating further theoretical work on paramagnons.

The experiments were carried out on oriented single crystals of NiF_2, which were of excellent optical quality and were generously supplied by Guggenheim. The light-scattering and temperature-control techniques are described elsewhere in detail.[1] An argon-ion laser (200 mW at 5145 Å), a Spex double monochromator, and the usual dc photoelectric detection scheme were employed. The temperature variation between 10 and 300°K was achieved using a flowing He or N_2 gas system. The sample temperature was monitored with a calibrated Pt resistor. Although the temperature could be maintained to within ±0.1°K over long periods, we estimate the measurement of the absolute temperature within the scattering volume to be accurate only to within ±2°K. For the lowest-temperature measurements (1.8°K) the sample was immersed in liquid He, and the He was pumped to a vapor pressure of 12.5 Torr.

NiF_2 is a rutile-structure canted-spin antiferromagnet with a transition temperature of $T_N=73$°K.[2] In the magnetic state the spins ($S=1$) align perpendicular to the c axis and not quite antiparallel to each other. This lack of antiparallelism gives rise to a weak ferromagnetic moment along the b axis and results in a lifting of the twofold degeneracy for long-wavelength magnons. However, as the Brillouin-zone boundary is approached, the magnon branches again become degenerate. This simplifies analysis of the two-magnon scattering in NiF_2. Group theory indicates that for the geometries observed experimentally (xz and yz) the magnons at the M, U, and R points in the Brillouin zone contribute most heavily to the light scattering.[3] This result is based on the fact that the two-magnon state responsible for the light scattering carries zero spin and is comprised of one magnon from each sublattice in the antiferromagnetic phase. Experimental verification of this assignment was obtained by observing spectra in magnetic fields (both parallel and perpendicular to the c axis) of up to 50 kOe. The two-magnon peak showed no splitting or shift in such fields. An experimental geometry permitting simultaneous observation of both one- and two-magnon scattering was used. Incident light was polarized along the c direction and light scattered at 90° was viewed in x and/or y polarization. The xz and yz spectra were identical within experimental error.

The spectra of Fig. 1 show the first-order scattering from a single zone-center magnon (I) at $\sim$31 cm^{-1}, as well as the second-order scattering from pairs of zone-boundary magnons (II). Referring to I, note that both its intensity and its frequency diminish as the temperature is increased toward T_N. This behavior is in accord with the earlier infrared-absorption observations of the zone-center magnon.[4] Although this long-wavelength

---

[1] P. A. Fleury and R. Loudon, Phys. Rev. **166**, 514 (1968).

[2] A. H. Cooke, K. A. Gehring, and R. Lazenby, Proc. Phys. Soc. (London) **85**, 967 (1965).

[3] R. Loudon (private communication); see also S. J. Joshua and A. P. Cracknell, J. Phys. **C2**, 24 (1969).

[4] P. L. Richards, Phys. Rev. **138**, A1769 (1965).

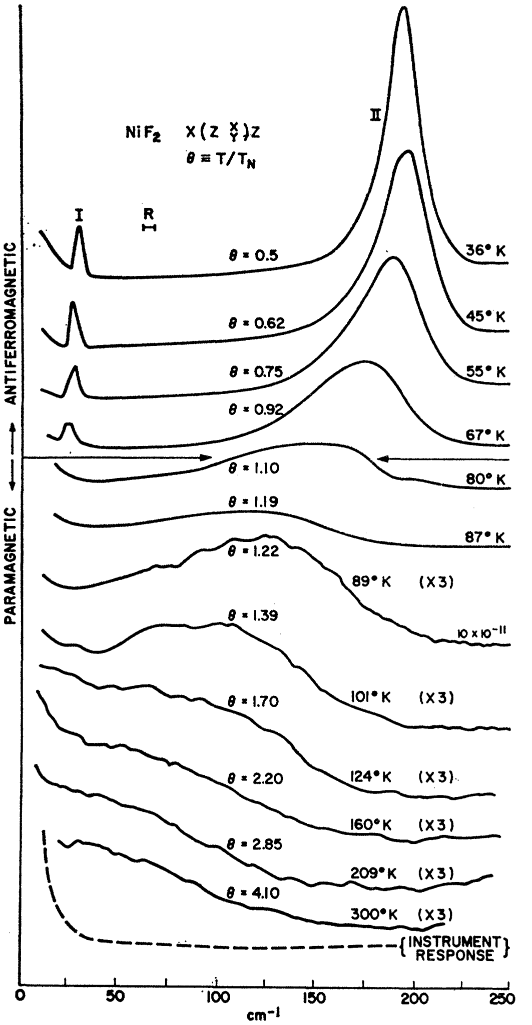

FIG. 1. Spectrum of magnetic light scattering in antiferromagnetic and paramagnetic NiF_2 ($T_N = 73°K$). Peak I is due to a single zone-center magnon and disappears with the disappearance of long-range order at T_N. Peak II is due to pairs of zone-boundary magnons and clearly persists well above T_N. Note the change in sensitivity for temperatures above 89°K. The instrument-response curve is appropriate to these more sensitive traces.

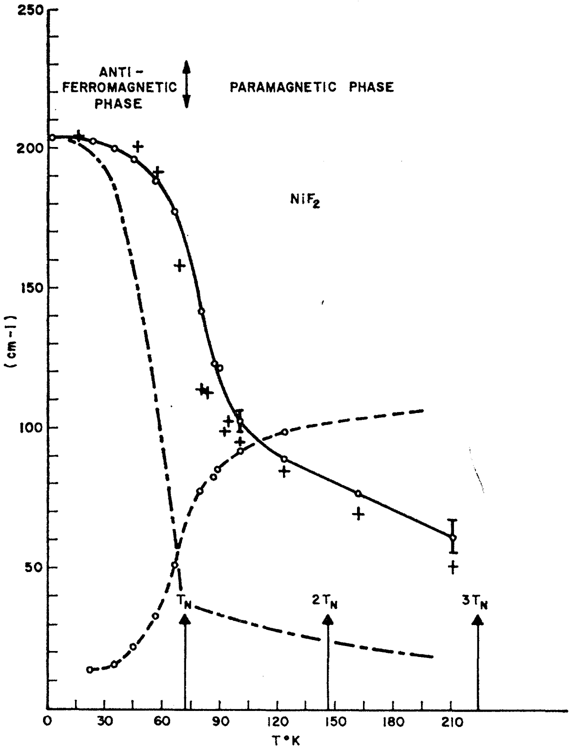

FIG. 2. Temperature dependence of various aspects of peak II. Solid line: observed frequency of peak II. Crosses: normalized integrated intensity of scattered light in peak II (arbitrary units). Dashed line: observed full width at half-maximum for peak II. Dot-dashed line: nearest-neighbor equal-time spin correlation function for $S = 1$ calculated in Ref. 7.

magnon can be seen at temperatures as high as $0.95T_N$, it completely disappears when T_N is exceeded and long-range order vanishes.

In contrast is the behavior of the two-magnon peak II. While it also decreases in frequency and intensity as the temperature is raised, it does not disappear above T_N. On the contrary, peak II persists above T_N and remains underdamped to at least $1.5T_N$. Magnetic scattering is evident even at 300°K ($4.1T_N$). The temperature behavior in Fig. 1 indicates not only that short-range magnetic order persists well into the paramagnetic phase, but also that the short-wavelength collective excitations of the paramagnetic phase are relatively long-lived and represent a continuous evolution from what were magnons in the antiferromagnetic phase.

The identification of peak II as a two-magnon feature resulting from paired zone-edge magnons, one on each of the opposite sublattices, is in agreement with the observation of magnetic field effects. Further, the frequency of the *M*-, *U*-, and *R*-point magnons inferred (slightly in excess of 100 cm^{-1}) is in good agreement with the estimates based on Moriya's theory.[5] Other experiments indicate the importance of magnon-magnon interactions in NiF_2, a subject we will discuss in a later publication.

The temperature dependence of the frequency of peak II is shown by the solid line in Fig. 2. In contrast to the one-magnon frequency which follows a modified Brillouin function and approaches zero at T_N, the two-magnon frequency decreases much more slowly and is still at about 75% of its zero-temperature value when T_N is reached. Perhaps more important, the integrated intensity of II behaves in a similar manner with temperature. The normalized integrated intensity is indicated by the crosses in Fig. 2.

After this work had been completed, the neutron

---

[5] T. Moriya, Phys. Rev. 117, 635 (1960).

scattering experiments of Martel *et al.*[6] in CoF_2 were brought to our attention. In addition to their intrinsic interest, these experiments when considered with ours illustrate the *complementary* information obtained by the two experimental techniques. We shall discuss this below. Martel *et al.*[6] observed inelastic neutron scattering from a single short-wavelength magnon in CoF_2 between 4.2 and 80°K. The transition temperature in CoF_2 is 38°K. Their results are similar to ours in that they find a continuous evolution of the scattering as the system evolves from the antiferromagnetic to the paramagnetic phase. There are some differences, however, which are likely to be significant. The frequency of their line falls off more quickly with temperature than does our II. If normalized in frequency to our values of $T=0$, their data would fall between our observed curve and the two-spin correlation calculation[7] shown in Fig. 2. Some of this difference is undoubtedly due to the difference between the magnetic behavior of NiF_2 and CoF_2 (the latter is considerably more complicated). We believe that the fact that different quantities are measured in the two experiments is perhaps more significant.

Because neutron scattering examines short-wavelength excitations in first order and light scattering does so in second order, the two techniques are sensitive to different spin correlation functions. It is well known that neutron scattering efficiencies (for one-magnon processes) are determined by two-spin correlation functions.[8] In two-magnon scattering (such as we observe), because the excitation produced consists of one magnon on each sublattice, the scattering is described by an interaction of the form

$$H^{\mathrm{II}}=\sum_{\mathbf{r},\mathbf{r}'}\sum_{i,j}G^{ij}(\mathbf{r}-\mathbf{r}')E_1{}^iE_2{}^jS^-(\mathbf{r},t)S^+(\mathbf{r}',t)\,,\qquad i,\,j=x,\,y,\,z\,,\quad(1)$$

where E_1 and E_2 are the incident and scattered fields, respectively, and $S^\pm$ are spin operators. The tensor $G^{ij}(\mathbf{r}-\mathbf{r}')$ is nonzero only for $\mathbf{r}=\mathbf{r}'+\boldsymbol{\delta}$, where $\boldsymbol{\delta}$ is a vector connecting nearest antiferromagnetic neighbors. The magnitude of G is determined by off-diagonal matrix elements of an excited-state exchange, and its i, j dependence is dictated by symmetry requirements of the space group of the crystal. The explicit form of H^{II} appropriate to $D_{2h}{}^{12}$ antiferromagnets is given in Ref. 1. Because H^{II} is bilinear in spin operators, it follows that the scattering rate is proportional to a four-spin correlation function. In particular,

$$\frac{d^2\sigma}{d\omega d\Omega}\propto\sum_{\mathbf{r}}\int_{-\infty}^{\infty}dt\,e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}\times\Big\langle\sum_{i,j,\delta}G^{ij}(\boldsymbol{\delta})S^-(\mathbf{r},t)S^+(\mathbf{r}+\boldsymbol{\delta},t)\times\sum_{l,m,\delta'}G^{lm}(\boldsymbol{\delta}')S^+(0,0)S^-(\boldsymbol{\delta}',0)\Big\rangle.\quad(2)$$

As seen from Eq. (2), the integrated intensity is determined by a four-spin equal-time correlation function. The results of light scattering and neutron scattering experiments are equivalent only if the four-spin correlation is trivially related to the two-spin function (for example, if magnon-interaction effects are negligible). However, this is not often the case, even in the zero-temperature approximation, as has been illustrated recently for the cubic antiferromagnet $RbMnF_3$.[9,10] The present experiments illustrate the need for extension of magnon-interaction theories not only to finite temperature in the magnetically ordered phase, but also beyond that into the disordered phase. They also suggest the desirability of coordinated light scattering and neutron scattering studies of the same systems over the same temperature ranges.

While the theory of neutron scattering in the paramagnetic phase is rather complete,[8] there remain several detailed points to be worked out with regard to light scattering in this phase. In the ordered phase the two-magnon line shape is determined by a suitably weighted magnon density of states[1] and magnon-magnon interactions. At high temperatures the effects of finite magnon lifetimes, of explicit temperature dependence of individual magnon frequencies, and of increasingly important magnon interactions all contribute to the frequency, width, and shape of the two-magnon line. To separate these contributions, further theoretical work is needed.

It is a pleasure to thank W. J. Brinkman, R. Loudon, and P.A. Wolff for helpful discussions, H. J. Guggenheim for the excellent single crystals of NiF_2, and H. L. Carter for technical assistance. I also thank J. P. Gordon and J. M. Worlock for comments on the manuscript.

---

[6] P. Martel, R. A. Cowley, and R. W. H. Stevenson, J. Appl. Phys. **39**, 1116 (1968).

[7] H. B. Callen and E. Callen, Phys. Rev. **136**, A1675 (1964).

[8] See, for example, M. F. Collins, J. Appl. Phys. **39**, 533 (1968).

[9] R. J. Elliott *et al.*, Phys. Rev. Letters **21**, 147 (1968).

[10] P. A. Fleury, Phys. Rev. Letters **21**, 151 (1968).