conversion in bulk condensed H_2 is significantly slower, i.e., ~6% per hour with complete conversion occurring over a period of weeks![15] For our thickest condensed layers (10 L) the conversion is slower than for the first adsorbed layer and we can initially observe more o-H_2 than observed in Figs. 1 and 2. This suggests that the conversion of orthohydrogen to parahydrogen likely involves a short range (magnetic) interaction of molecular H_2 with the metal surface. Clearly, this conversion process remains to be more completely understood.

In summary, we have observed pure rotational and rotational-vibrational excitations of H_2 and D_2 adsorbed on Ag at ~10 K. Our results show unhindered rotations and an internuclear separation slightly shorter but within 2% of the condensed phase. This provides evidence for a physisorbed state which does not feel the anisotropies or energy barriers along the surface. The adsorbed H_2 has also been converted to the paranuclear spin state.

This work was partially supported by the U. S. Office of Naval Research.

[1]J. K. Norskov, A. Houmoller, P. K. Johansson, and B. I. Lundqvist, Phys. Rev. Lett. 46, 257 (1981).
[2]P. Cremaschi and J. L. Whitten, Phys. Rev. Lett. 46, 1242 (1981).
[3]P. K. Johansson, Surf. Sci. 104, 510 (1981).
[4]H. Hjelmberg, B. I. Lundqvist, and J. K. Norskov, Phys. Scr. 20, 192 (1979).
[5]A. R. Gregory, A. Gelb, and R. Silbey, Surf. Sci. 74, 497 (1978).
[6]J. E. Demuth, K. Christman, and P. N. Sanda, Chem. Phys. Lett. 76, 201 (1980).
[7]Ph. Avouris and J. E. Demuth, J. Chem. Phys. 75, 4783 (1981).
[8]S. F. Wong and G. J. Schulz, Phys. Rev. Lett. 32, 1089 (1974).
[9]U. Fink, T. A. Wiggins, and D. H. Rank, J. Mol. Spectrosc. 18, 384 (1965).
[10]B. P. Stoicheff, Can. J. Phys. 35, 730 (1957).
[11]H. P. Gush, W. F. J. Hare, E. J. Allin, and H. L. Welsh, Can. J. Phys. 38, 176 (1960).
[12]E. J. Allin, T. Feldman, and H. L. Welsh, J. Chem. Phys. 24, 1116 (1956).
[13]G. Herzberg, *Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1950).
[14]See, for example, H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (Wiley, New York, 1944).
[15]I. F. Silvera, Rev. Mod. Phys. 52, 393 (1980).
[16]S. K. Sharma, M. K. Mao, and P. M. Bell, Phys. Rev. Lett. 44, 886 (1980).
[17]T. R. Knowles and H. Suhl, Phys. Rev. Lett. 39, 1417 (1977).
[18]D. King, Crit. Rev. Solid State Mater. Sci. 7, 167 (1978).
[19]Room temperature H_2 consists of 68% $J=1$, 14% $J=0$, 11% $J=2$, and 8% $J=3$, plus higher rotational states.

Magnetic Energy Fluctuations: Observations by Light Scattering

K. B. Lyons and P. A. Fleury
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 30 November 1981)

The first observations of magnetic energy fluctuations by light scattering are reported. The spectra observed in antiferromagnetic $KNiF_3$ are strongly polarized, mildly q dependent, but strongly temperature dependent near $T_N = 248.5$ K. The observed line shapes exhibit two characteristic frequencies, one less than 0.6 GHz and the other between 5 and 15 GHz, depending on temperature.

PACS numbers: 78.40.Ha, 75.30.Ds, 78.20.Ls

Inelastic light scattering in magnetic solids has traditionally been employed to measure the behavior of spin waves and of spin-wave pairs with near-zero total momentum.[1] From such measurements accurate values for parameters in the spin Hamiltonian of ferromagnets, ferrimagnets, and antiferromagnets have been obtained.[2,3] In addition to these effects, it should in principle be possible to observe directly the fluctuations in the spin-wave density, or the magnetic energy, through a process analogous to the phonon density fluctuation scattering recently proposed and observed in phonon systems.[4]

In this Letter we report the first observations by light scattering of this type of process. As shown in Fig. 1, the light scattering spectra, ob-

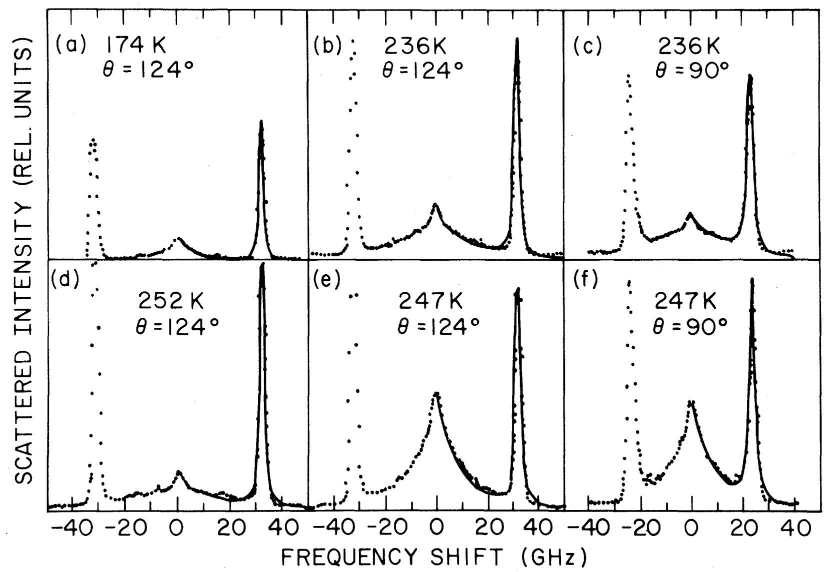

FIG. 1. Fully polarized spectra obtained at two scattering angles in $KNiF_3$ at the temperatures indicated. Full scale is 5000 cps. The transition is at T_N = 248.5 K. The points represent the data while the curves show the fit discussed in the text.

tained in $KNiF_3$, are polarized and exhibit striking temperature dependence near T_N=248.5 K. The spectral line shape is complex and strongly temperature dependent near T_N, comprising two quasielastic relaxation components in addition to the usual longitudinal acoustic (LA) mode. This scattering, which disappears rapidly above T_N, thus demonstrating its magnetic origin, was studied over the temperature range 150–260 K at two scattering angles. The (depolarized) one-magnon scattering was also observed over the temperature range 20–245 K. These latter results will be discussed more fully in a later publication.

Potassium nickel fluoride, $KNiF_3$, a cubic perovskite (O_h^1), remains cubic but orders antiferromagnetically below T_N= 248 K.[5] The sublattice magnetization lies along the cubic axes, and, in the absence of aligning strain or magnetic fields, will give rise to domains. $KNiF_3$ was chosen for the present study because (1) its cubic O_h^1 symmetry forbids first-order Raman scattering from phonons; (2) second-order Raman scattering from phonons is very weak; (3) the spin Hamiltonian is accurately Heisenberg,[5] with a large exchange (J= 71 cm^{-1}) and small anisotropy ($E \approx 0.025$ cm^{-1}); and (4) the two-magnon sum scattering is strong.[2] One-magnon scattering[6] appears only in completely depolarized geometries and is thus separable from the polarized energy fluctuation scattering discussed below.

The spectra are excited using 50–70 mW of linearly polarized 5145-Å light from a single-mode Ar^+ laser, tuned to an I_2 absorption line. The scattered light is analyzed by a tandem pressure-scanned Fabry-Perot interferometer[7] (Γ_{inst} = 0.9 GHz, free spectral range 690 GHz; all widths are given here as half width at half maximum). The scattered light traverses an I_2 cell which reduces the elastic component by a factor of 2×10^8, while passing up to 15% of the inelastically scattered light. Computer analysis is used to restore the inelastic spectral profile for $|\Delta\nu| \gtrsim 0.5$ GHz. The $KNiF_3$ sample is cut into a parallelepiped with laboratory axes a:b:c = (210):(1$\bar{2}$0):(001). No magnetic fields or deliberate stresses are applied; hence, the sample is multidomain below T_N. The sample is mounted with silver paste (b axis vertical) in vacuum on the Cu cold finger of a variable-temperature cryostat. Absolute sample temperature is accurately known to ~1.0 K, while temperature changes are controlled to better than 0.02 K. Laser heating at the scattering volume is less than 0.8 K, and the data displayed below are corrected correspondingly.

In $a(ca)c$ and $a(cb)c$ geometries we observed the one-magnon line up to $T = T_N - 2$ K. Its frequency remains above 24 GHz, as expected for our finite q (θ= 90°), and the peak remains underdamped. Its integrated intensity extrapolates linearly to zero at T_N.

Typical magnetic energy fluctuation (bb) spectra are shown in Fig. 1. Below ~150 K there is virtually no scattering evident between the peaks of the LA doublet. When first measurable with any degree of accuracy ($T \approx 150$ K), its width is about 5 GHz. This width increases with T and a two-component structure becomes obvious, especially in the backscattering geometry [$\theta = 124°$, $q \parallel (001)$, Figs. 1(b), 1(e), and 1(d)]. The peak scattering intensity increases sharply in the immediate vicinity of T_N (becoming comparable to that from the LA modes) and exhibits rapid changes in its line shape [Figs. 1(b) and 1(e)]. Immediately above T_N [Fig. 1(d)], the intensity drops so sharply that intensity changes are easily observable for temperature changes as small as 0.03 K just above the maximum. (These changes are not due to changes in the absorption at 5145 Å, which increases smoothly from ~4% at 150 K to ~10% near T_N, exhibiting no anomaly at the transition.) The temperature of this drop agrees within 0.2 K with the value for T_N obtained by extrapolating the one-magnon intensity to zero. The spectra in right-angle scattering geometry, shown in Figs. 1(c) and 1(f), exhibit very similar profiles, except for the movement of the LA mode caused by the change in q.

It is clear that these spectra exhibit three characteristic frequencies. The fits displayed in Fig. 1 employ two components of a Debye form

$$S_{\text{Debye}} = A_i \Gamma_i^2 / (\omega^2 + \Gamma_i^2) \qquad (1)$$

for the central components, where A_i is the peak amplitude and Γ_i is its width, and a damped harmonic oscillator function to describe the LA doublet. The width of the narrow component Γ_1 was never observed to vary significantly, and hence it was fixed at 1.5 GHz (see below). While the three parameters describing the LA phonon peak exhibit no significant anomalies, those describing the Debye components exhibit striking changes near T_N. The width of the broader one, Γ_2, shown in Fig. 2, is virtually identical for the two scattering geometries employed, with a dip of some 40% at T_N. A sharp maximum in the intensity A_2 accompanies this minimum in Γ_2, which, although shown displaced in Fig. 2 for clarity, actually occurs at the same temperature within 0.04 K. As shown, the amplitude scales as $A_2 \sim q^2$.

The narrow component carries a small fraction of the total integrated intensity (2%–4%). Its amplitude A_1 exhibits a more gradual peak at T_N, but has a value in backscattering which is twice that observed at right angles. This corresponds roughly to a q^4 dependence. The apparent deconvolved width of the peak, ~0.6 GHz, is sufficiently narrow compared to the main I_2 absorption that much of the scattered light in that component is absorbed. In that case, we cannot distinguish changes in the true amplitude A_0 from changes in the true width Γ_0. The value of 0.6 GHz obtained from the width Γ_1 represents only an upper limit on Γ_0. The *observed* amplitude A_1 would scale as $A_0\Gamma_0^2$ for a peak substantially narrower than 0.5 GHz. If both the integrated intensity ($A_0\Gamma_0$) and the linewidth were to scale as q^2 that would roughly explain the observed q dependence of A_1. While other possible explanations cannot be excluded, this particular one is consistent with theoretical ideas outlined below.

The theoretical interpretation of the spectra must account for the very large polarization ratio (> 20) observed and for the temperature dependence of both the intensity and line shape. All of

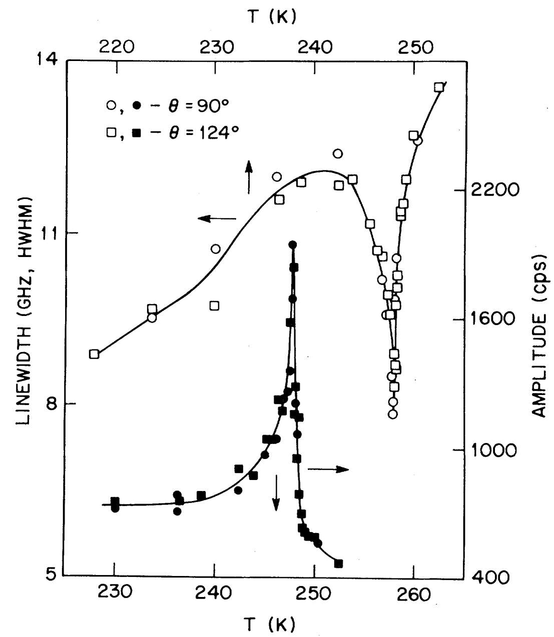

FIG. 2. Width Γ_2 (upper and left scales, open points) and the peak amplitude A_2 (lower and right scales, solid points) resulting from the fits to spectra as in Fig. 1, in the vicinity of $T_N = 248.5$ K. The points show the data for the two scattering angles ($\theta = 90°$, $q_1 = 1.73 \times 10^5$ cm^{-1}; $\theta = 124°$, $q_2 = 2.16 \times 10^5$). The lines are guides to the eye. The values at 150 K are ~5 GHz and ~300 cps, respectively. Note that the ordinate scales do not extend to zero and the abscissas are displaced 10.0 K. No correction has been made for Γ_{inst}, nor for the sample absorption, but the amplitudes are scaled to q^2 and corrected for reflection.

these lie in contrast to the behavior of the previously observed two-magnon sum scattering,[2] which has been shown to be predominantly of Γ_3^+ symmetry, and hence active in both polarized and depolarized geometries. In addition, the two-magnon sum scattering exhibits no singular temperature dependence in either its line shape or its intensity near T_N. While preliminary theoretical calculations[8] reproduce some features of our data, notably the strong polarization selection evidenced by the spectra, the fact that no explanation can be given on this basis for the q independence of the peak width nor for the singular behavior near T_N leads us to believe that the new scattering reported here is of more complex origin than suggested by this simple mechanism.

A more general picture which implicitly incorporates magnon lifetimes and interactions, as well as implying polarized scattering,[9,10] involves magnetic energy fluctuations. If the spin-lattice relaxation time significantly exceeds the spin-spin relaxation time, then the magnetic energy can be regarded as a quasiconserved quantity. This led Heller[9] to propose that two time scales would appear in the system: (1) a short one τ_s for local (collisionless) spin-spin relaxation and (2) a long one for nonlocal (i.e., collision-dominated diffusion) relaxation within the isolated spin system. The spectral manifestation of this time-scale separation would appear as a diffusive ($\Gamma \sim q^2$) peak superimposed on a *q-independent* peak, with a width given by the inverse spin-spin relaxation time. We note the analogy here with the case of "entropy fluctuation" and "phonon density fluctuation" scattering in ordinary phonon systems.[11] In addition, Heller suggests that τ_s should diverge as $T \rightarrow T_N$. While these ideas are qualitatively consistent with our observations, no microscopic or quantitative calculations are presently available for the magnitudes of the characteristic times or their temperature dependences.

Alternatively assuming that the light scattering is *only visible* via the spin-lattice coupling, Reiter[10] has predicted a single q-independent peak with a width given by the inverse *spin-lattice* relaxation time. Since we see no evidence of any coupling between the acoustic modes and the magnetic energy fluctuations, the assumption of dominant spin-lattice coupling appears inapplicable to $KNiF_3$. It should be noted, however, that interactions with the lattice cannot be ignored *a priori*. In particular, the role of ordinary entropy fluctuations in the narrow component cannot be quantitatively assessed, since the relevant thermal parameters of $KNiF_3$ as well as the true width Γ_0 for the narrow component are not yet available.

While the detailed theory for these new observations remains to be developed, there can be no doubt that these experiments have revealed anomalous, singular magnetic light scattering due to processes occurring on time scales which are slow compared to characteristic magnon frequencies. Such measurements should provide new information on spin-relaxation processes. These and similar phenomena should be observable in other three-dimensional systems and in magnetic systems of lower symmetry and lower dimensionality, as well as in mixed or diluted magnetic crystals.

The authors acknowledge helpful theoretical discussions with M. Cottam and B. Halperin. We also thank H. J. Guggenheim for samples and H. L. Carter and T. J. Negran for experimental assistance.

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

[2] S. R. Chinn, H. J. Zeiger, and J. R. O'Connor, Phys. Rev. B 3, 1709 (1971).

[3] R. E. Pisarev, P. Moch, and C. Dugautier, Phys. Rev. B 7, 4185 (1973).

[4] K. B. Lyons and P. A. Fleury, Phys. Rev. Lett. 37, 161 (1976).

[5] K. Hirakawa, T. Hashimoto, and K. Hirakawa, J. Phys. Soc. Jpn. 16, 1934 (1961).

[6] P. Moch and C. Dugautier, in *Proceedings of the Ninth International Conference on Magnetism, Moscow, U.S.S.R., 1973* (Nauka, Moscow, U.S.S.R., 1974), Vol. 3, p. 185.

[7] K. B. Lyons and P. A. Fleury, J. Appl. Phys. 47, 4898 (1976).

[8] M. G. Cottam, private communication.

[9] P. Heller, Int. J. Magn. 1, 53 (1970).

[10] G. F. Reiter, Phys. Rev. B 13, 169 (1976).

[11] R. A. Cowley and C. J. Coombs, J. Phys. C 6, 143 (1973).