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MAGNONS AT LOW AND HIGH TEMPERATURES IN THE PLANAR ANTIFERROMAGNET K_2NiF_4

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The spin-wave spectrum of K_2NiF_4 has been measured at 5.0°K and found to be extremely anisotropic with no measurable dispersion in the direction perpendicular to the NiF_2 planes. A study of the temperature dependence of the two-dimensional magnons shows that even relatively long-wavelength spin waves ($\lambda \approx 110$ Å) show little renormalization or lifetime effects up to $\approx 1.1T_N$.

The study by Birgeneau, Guggenheim, and Shirane[1] of the quasielastic scattering of neutrons on the group of compounds typified by K_2NiF_4 has recently provided definitive proof of their two-dimensional character. In particular, long-range two-dimensional correlations were observed to exist over a wide range of temperatures above the phase transition temperature ($T_N = 97.1$°K in K_2NiF_4). From the form of quasielastic scattering above and below T_N the investigators concluded that in K_2NiF_4 the phase transition at 97.1°K is two-dimensional in nature, the three-dimensional aspects being essentially redundant. More recent quasielastic measurements[2] show that above T_N the diffusive scattering is associated entirely with the z-z component of the wave-vector-dependent susceptibility $\chi^{\alpha\alpha}(\vec{q})$, thus indicating that even in the paramagnetic regime the anisotropy is playing a crucial role. In order to understand the nature of the phase transition it is necessary to have quantitative information about both the isotropy of the Hamiltonian and the relative size of intra- and interplanar interactions; these may be determined through a study of the magnons at low temperatures. In addition, considerable insight into the spin dynamics may be obtained by studying the thermal evolution of the magnons around T_N; it might be anticipated that this could be extremely unusual in a two-dimensional near-Heisenberg system. We have therefore undertaken a detailed study of the magnons in K_2NiF_4. In this Letter we report the results of this study at low temperatures (5°K) together with some preliminary measurements of the magnons around T_N.

From the two-dimensional character of K_2NiF_4, a highly anisotropic spin-wave spectrum is expected with measurements in the c direction giving an indication of interplanar exchange. The magnetic structure[3] is shown in Fig. 1 where the planar behavior is evident in that the NiF_2 planes are separated from one another by two KF planes. Furthermore, within the molecular-field approximation, there is no net coupling between nn planes in the Néel state. This structure results in two domains as the body-centered spin in Fig. 1 can be up or down.

Because of the existence of two domains, measurements were by necessity made simultaneously in both the [100] and [010] zones. The spin-wave spectrum along $[\zeta, 0, 0]$ and $[0, \zeta, 0]$ are the same if only intraplanar exchange exists. The spin-wave energy for intraplanar magnons has been obtained using the expression given by Keffer[4] for a uniaxial two sublattice antiferromagnet; for $[\zeta, 0, 0]$ the energies are

$$E(q_x) = \{[g\mu_B H_A - 4J_1 + 4(J_2 + 2J_3)\sin^2\tfrac{1}{2}q_x a]^2 - 16J_1^2\cos^2\tfrac{1}{2}q_x a\}^{1/2}. \qquad (1)$$

The above assumes $S=1$ and is written for exchange between the first three nearest neighbors in the plane with $H_{ij}=-J_{ij}\vec{S}_i\cdot\vec{S}_j$.

The crystal utilized in the present measurements is approximately 0.5 cm^3 in volume with a full-width at half-maximum mosaic of 30 min. The magnon dispersion was measured at 5.0°K on a triple-axis spectrometer emplaced at the Brookhaven high-flux-beam reactor. Pyrolytic graphite was used for both monochromator and analyzer with 20-min collimation before and after the sample. In-pile and detector collimation and the initial neutron energy were varied as needed in order to achieve the best focusing conditions of the instrumental resolution with the dispersion curve.[5]

The dispersion curve in the $[\zeta, 0, 0]$ direction is shown in Fig. 2 where points on the steep part of the curve were measured with constant-E scans. All measurements were taken from magnetic Bragg points of the [010] zone. Even though the two zones give rise to two-magnon surfaces, at no point was there any more than one magnon observed. This was particularly evident at [0.45, 0, 0] near the zone boundary, where measurements were made with the constant $\vec{Q}$ technique with the spectrometer in a well-focused condition. Because of this sharp focusing around [0.45, 0, 0] it was advantageous to study the dispersion in the c direction along $[0.45, 0, \zeta]$. The results are shown in Fig. 2. Quite remarkably, there is no measurable dispersion at all. All points gave values of 38.1 ± 0.1 meV. A similar lack of dispersion was also found along the $[0, 0, \zeta]$ direction, although with higher relative uncertainty.

Because of this complete lack of dispersion in the c direction, we may use Eq. (1) to analyze the results. For measurements away from the zone center, Eq. (1) can be expanded if $J_2+2J_3 \ll J_1$ to give

$$E(q_x)=4\left|J_1\sin\frac{q_xa}{2}\right|\left(1-\frac{J_2+2J_3}{J_1}\right)+\cdots. \tag{2}$$

As a result, the analysis gives $J_1[1-(J_2+2J_3)/J_1] = -9.68\pm0.03$ meV with the proviso that $J_2+2J_3 \ll J_1$. Utilizing the accurate antiferromagnetic resonance of 2.37 meV for the $\vec{q}=0$ magnon energy,[6] the anisotropy energy is determined to be $g\mu_BH_A=0.073$ meV. It should also be noted that a full least-squares fit allowing J_1, J_2+2J_3, and $g\mu_BH_A$ to vary freely gives $J_2+2J_3=0$ within the errors, but with J_1 and J_2+2J_3 very strongly correlated.

It is of interest to estimate the strength of interplanar exchange consistent with our observations. Measurements along $[0.45, 0, \zeta]$ are of high relative accuracy; the magnon energy is 38.1 meV while the dispersion is most certainly less than ±0.14 meV. If we assume that the nearest-neighbor interplanar exchange J_1' is much less than J_1 we obtain away from the zone center

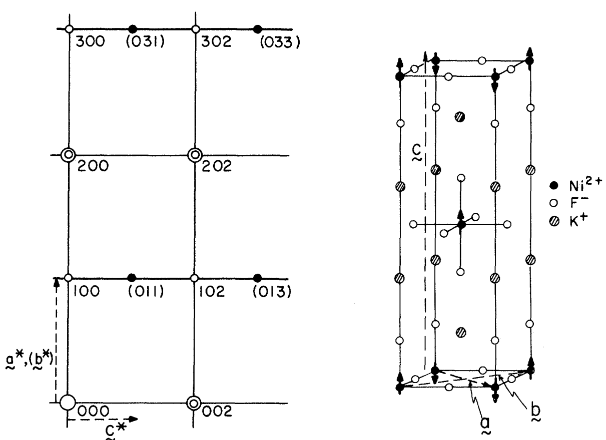

FIG. 1. Chemical and magnetic structure of K_2NiF_4. Inverting the central spin exchanges the a and b axes. The reciprocal lattice displays both the [010] and [100] magnetic zones. The nuclear Bragg peaks are indicated by double circles. The thick lines indicate the vicinity in which two-dimensional critical scattering is observed.

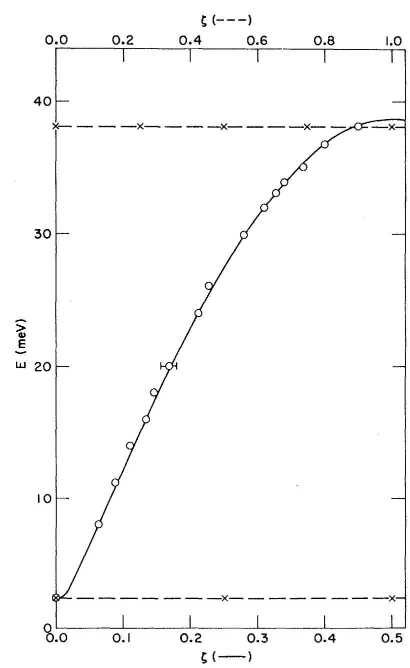

FIG. 2. Magnon dispersion curve in the [010] zone. The solid line is for $[\zeta, 0, 0]$, while the dashed lines are for $[0, 0, \zeta]$ at 2.4 meV and $[0.45, 0, \zeta]$ at 38.1 meV.

for $[q_x, 0, q_z]$ magnons

$$E(q_x, q_z) = 4\left|J_1 \sin\frac{q_x a}{2}\right|\left(1-\frac{J_2+2J_3}{J_1}\right) \times\left(1+\frac{J_1'}{J_1}\cos\frac{q_z c}{2}\right)+\cdots. \quad (3)$$

$E(q_y, q_z)$, on the other hand, has no first-order dependence on J_1'. As there is no dispersion to within 1 part in 270 for the mean energy of $E(q_x, q_z)$ and $E(q_y, q_z)$, we have $J_1 > 270J_1'$.

We now consider the temperature evolution of the magnon energies and lifetimes. Previous experiments in three-dimensional antiferromagnets have shown that as T_N is approached the spin-wave energies are considerably renormalized and the half-widths become comparable with the energy itself.[7] Nevertheless, at short wavelengths, magnonlike propagating modes are still in evidence above T_N. In K_2NiF_4, because of the anomalously wide temperature region over which there are long-range two-dimensional correlations above T_N, we might expect more dramatic behavior. Measurements of the pure $\vec{q}=0$ mode have been carried out by Birgeneau, DeRosa, and Guggenheim[6] in K_2NiF_4 using antiferromagnetic resonance and these show entirely conventional behavior; the antiferromagnetic resonance energy drops to zero like the sublattice magnetization and the linewidth increases markedly so that the mode is barely resolvable at 85°K.

We have carried out measurements of the temperature dependence of the magnons at several wave vectors. In Fig. 3 the results of constant-energy scans at 7 meV in the vicinity of $\vec{q}=(0.05, 0, 0)$ are shown. This wave vector is equivalent to a wavelength of ≈110 Å. From the figure it may be seen that there is no measurable change in $\vec{q}$ or the width up to 105°K, that is, to $\approx 1.1T_N$. Thus not only do these relatively long wavelength magnons remain well defined above the phase transition, they are, in fact, indistinguishable from their counterparts at $T=0$°K. Put another way, it appears that in K_2NiF_4, low-temperature spin-wave theory gives a good description of the magnon energies away from $\vec{q}=0$ at $1.1T_N$. Finally, by 146°K the spin-wave mode has merged with the longitudinal diffusive mode and is no longer resolvable.

It is now possible to understand the quasielastic measurements above T_N. Since the transverse susceptibility retains a spin-wave character over most of the zone above T_N, no appreciable Lorentzian diffuse scattering is expected as

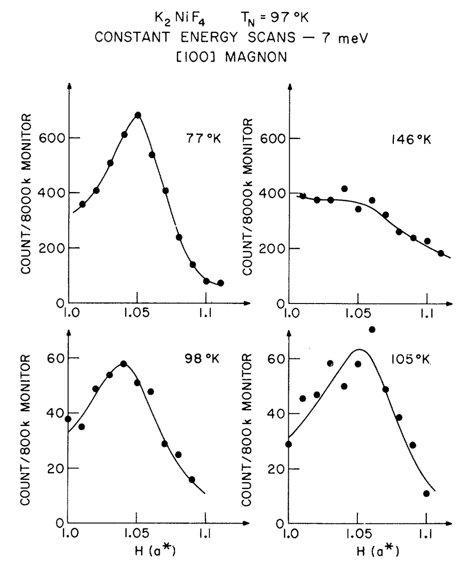

FIG. 3. Temperature dependence of [0.05, 0, 0] magnon. Note the change in counting statistics between the upper and lower scans.

indeed none is observed. The longitudinal susceptibility, on the other hand, is diffusive in form and $\chi^{zz}(0)$ is observed to diverge at T_N as expected for an anisotropic antiferromagnet.

In summary, we have carried out a detailed study of the magnons in K_2NiF_4 in the [1, 0, 0], [0, 1, 0] zones at 5°K together with a preliminary study of the thermal evolution of the magnons. At 5°K the observed magnon dispersion relations can be accurately described by simple two-dimensional spin-wave theory employing nearest-neighbor Heisenberg interactions together with an anisotropy field 500 times smaller than the exchange field. The lack of dispersion in the c direction necessitates that the interplanar exchange field be at least a factor of 270 smaller than the intraplanar interactions. Thus the dynamics show that K_2NiF_4 is very close to being a pure two-dimensional Heisenberg system although the small anisotropy does play a crucial role in the paramagnetic regime (and assumedly in the phase transition itself[1,2]). The temperature dependence of the magnons is also quite unusual in that up to $\approx 1.1T_N$ no appreciable thermal effects are seen for magnons with wavelengths as long as 110 Å. It is clear that this latter result calls for much more detailed study. In particular, it would be very interesting to compare the evolution of the magnon energies and lifetimes with the corresponding evolution of the longitudinal correlation length. Such experiments are now underway.

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MULTIPLET SPLITTING OF CORE-ELECTRON BINDING ENERGIES IN TRANSITION-METAL IONS*

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X-ray photoelectron spectra indicate core-electron binding-energy splittings of ~6 eV for the 3s levels in MnF_2, MnO, and FeF_3, and less pronounced effects on the 3s levels in MnO_2 and Fe metal. These splittings are considerably reduced from free-ion predictions but agree well with calculations for Mn in a cluster environment. The 3p multiplet splittings are shown to behave in a quantitatively different fashion.

In any atomic system with unpaired valence electrons, the exchange interaction affects core electrons with spin up and spin down differently. This interaction is responsible for the well-known core-polarization contributions to magnetic hyperfine structure.[1] The binding energies of core electrons will also be affected. For example, unrestricted Hartree-Fock (UHF) calculations predict large splittings in the core-electron energy eigenvalues of transition-metal ions[2] (~12 eV for the 3s level of atomic iron), and it has been pointed out that these splittings should be reflected in measured binding energies.[3] Using x-ray photoelectron spectroscopy (XPS) such splittings were sought in core-level peaks from iron and cobalt metal, but with negative results.[3] Recently, splittings of ~1 eV have been observed in the 1s-derived photoelectron peaks of the paramagnetic molecules O_2 and NO.[4] We report here the first observation of large effects in the 3s-like levels of Mn and Fe in various magnetic solids. The splittings are ~6 eV and considerably reduced from free-ion predictions,[2] in agreement with recent UHF molecular orbital calculations for the MnF_6 cluster.[5] Certain extra peaks in the 3p region provide evidence for large splittings of the 3p levels in these solids. In contrast to the 3s splittings, which may be interpreted from either an exchange-polarization or multiplet-structure viewpoint, the 3p splittings do not correspond to any picture based solely on exchange polarization in the UHF model.[6]