SUBLATTICE MAGNETIZATION OF QUADRATIC LAYER ANTIFERROMAGNETS

H. W. de Wijn, R. E. Walstedt, L. R. Walker, and H. J. Guggenheim
Bell Telephone Laboratories, Murray Hill, New Jersey 07974
(Received 26 February 1970)

The temperature variation of sublattice magnetization in the quadratic layer antiferromagnets K_2NiF_4 and K_2MnF_4 has been determined by measuring the NMR frequency of out-of-layer ^{19}F nuclei in these compounds. The results are found to agree with a simple two-dimensional spin-wave theory for $T \lesssim T_N/2$, with T_N = Néel temperature. Some evidence is found for residual exchange coupling between second-neighbor layers in K_2NiF_4; upper limits for such coupling are set. Evidence is also presented for a large zero-point spin reduction in K_2NiF_4.

Spin-wave excitations in the antiferromagnetic layer-structure compounds K_2NiF_4 and K_2MnF_4 are now believed to be essentially two dimensional. Legrande and Plumier[1] first showed that in K_2NiF_4 antiferromagnetic ordering takes place within each quadratic layer and noted that the magnetic interaction of adjacent layers is largely canceled by symmetry. Birgeneau, Guggenheim, and Shirane[2] have given definite evidence that the only short-range order above T_N is two dimensional; ordering in the third dimension occurs parasitically for $T \leq T_N$. Neutron studies of the magnon dispersion in K_2NiF_4[3] have also demonstrated the weakness of interlayer coupling. To further establish these conclusions and at the same time examine the limits of applicability of a simple spin-wave theory to these systems we have undertaken precise measurements of the temperature variation of sublattice magnetization. We find (1) excellent agreement with spin-wave theory appropriate to the quadratic layer for $T \lesssim T_N/2$, (2) some indication of a residual three-dimensional effect in K_2NiF_4 with upper limits for exchange coupling between second-neighbor layers, and (3) evidence for a large zero-point spin reduction in K_2NiF_4.

The technique used is the well-known one of tracking the Larmor frequency in zero applied field of ^{19}F nuclei adjacent to the magnetic ions. Measurements of the ^{19}F NMR frequency were carried out using the pulse method on multicrystalline specimens of K_2NiF_4 and K_2MnF_4 and on a single crystal[4] of K_2NiF_4. Results from the two specimens of K_2NiF_4 agreed within experimental accuracy. The ^{19}F nuclei resonated were those of nearest-neighbor ligand ions situated 2 Å on either side of a given antiferromagnetic plane. Temperature measurement and control were accomplished by means of pumped liquid He, H_2, and N_2, where applicable, or with a system utilizing a continuous stream of cold He gas. In the latter case the temperature was monitored and regulated with a feedback arrangement employing Ge resistance thermometers, calibrated with a Pt resistance thermometer. The accuracy of measured specimen temperatures is 0.5% or 0.2°K, whichever is less. The ^{19}F NMR frequency $f(T)$ was measured over the ranges $1.5 \leq T \leq 36°K$ for K_2MnF_4 ($T_N = 45 \pm 1°K$[5]) and $1.5 \leq T \leq 91°K$ for K_2NiF_4 ($T_N = 97.1 \pm 0.1°K$[2]) with a relative accuracy of 2×10^{-5} at the lowest temperatures, increasing to 2×10^{-4} at $\sim T_N/2$ (Fig. 1).

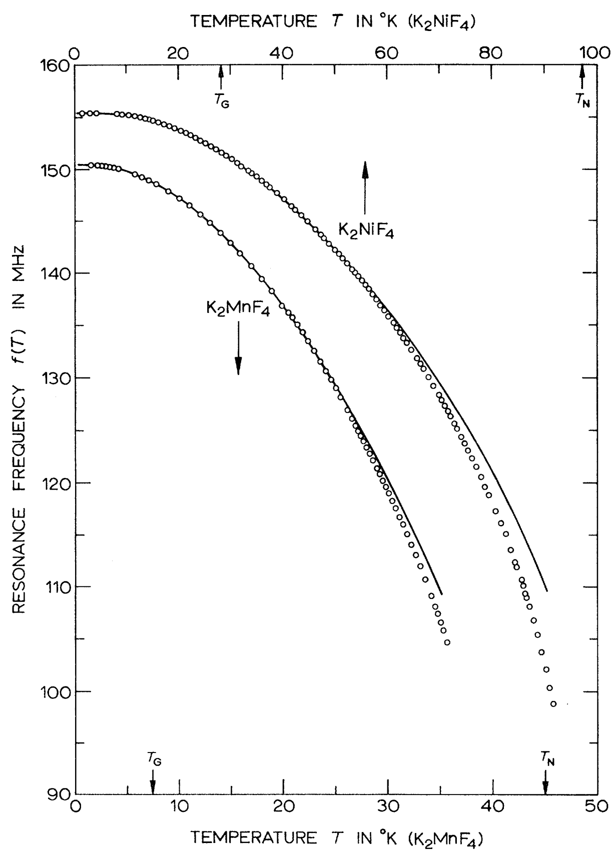

FIG. 1. The nuclear magnetic resonance frequency $f(T)$ of the ^{19}F out-of-layer nuclei in K_2NiF_4 and K_2MnF_4 versus the temperature T. T_G and T_N denote the gap and Néel temperatures, respectively. The solid curves are calculated from spin-wave theory as described in the text.

The accuracy of the frequency measurements was limited by the NMR linewidths where $T_2^* \approx 5$ μsec at low temperatures for both compounds. As the temperature approached T_N the resonance lines broadened rather abruptly and became unobservable. This broadening is thought to be homogeneous and may be similar to that observed in Mössbauer studies of the isomorphic Rb_2FeF_4.[6]

The dominant exchange interaction in these systems is known to be that between nearest neighbors (J_1).[3] The relative size of interactions with second or third neighbors (J_2 or J_3) is of the order of 1 %.[7] We have therefore carried out our data analysis in terms of a single effective nearest-neighbor exchange constant J. For small J_2 and J_3 this leads to minor errors in the computation at high temperatures. Interlayer coupling is neglected at the outset. We have calculated the decrease with temperature of the sublattice magnetization $\Delta(T) = \langle S_z \rangle_{T=0} - \langle S_z \rangle = S - \Delta_0 - \langle S_z \rangle$ exactly from noninteracting spin-wave theory for the nearest-neighbor exchange model using a computer integration over the first Brillouin zone.[8] Here Δ_0 is the zero-point spin reduction. We further find that $\Delta(T)$ is represented to within 2 % for $T \leq E_g/k_B$ and to within ~10 % over the temperature ranges studied by the analytic expression

$$\frac{-(1+\alpha)k_B T \ln[1-\exp(-E_g/k_B T)]}{2\pi S|J|}, \tag{1}$$

where $E_g = k_B T_G$ is the spin-wave gap energy and $\alpha = E_g^2/32S^2J^2$. This is derived by expanding the trigonometric functions in the dispersion relation to order $\vec{k}\cdot\vec{k}$ and integrating to $|k| = \infty$.[9] In the same approximation when J_2 and J_3 are significant, the single exchange parameter J in the denominator of Eq. (1) is replaced by $J_1 - 2J_2 - 4J_3$. It is reasonable to suppose that for small J_2 and J_3 the single J which we use in the exact theory is essentially $J_1 - 2J_2 - 4J_3$.

In the calculations described above, the anisotropy energy has been assumed to be $\vec{k}$ independent. This assumption has been checked for K_2MnF_4, where the anisotropy is predominantly dipolar in origin.[5] Inclusion of the full $\vec{k}$ dependence[10] was found to alter $\epsilon(\vec{k})$ by only 0.2 %, and is therefore negligible for our purposes. We believe that a similar conclusion holds for the predominant single-ion[11] and anisotropic exchange contributions to anisotropy in K_2NiF_4.

Fourth-order corrections of the sort discussed by Oguchi[12] give corrections to spin-wave theory which are independent of k, and which, in the cases at hand, are essentially independent of temperature.[13] Thus the form of the above results is unaltered by these corrections. However, because the low-temperature behavior is primarily determined by E_g, it is expedient to include the temperature dependence of this quantity.

In fitting our data with the theory we express the ^{19}F frequency as

$$f(T) = f(0)[1 - C\mathcal{L}(T)], \tag{2}$$

where $C = (1+\alpha)k_B/2\pi S(S-\Delta_0)|J|$, and $\mathcal{L}(T)$ is a function of temperature which asymptotically approaches

$$\mathcal{L}(T) \simeq T \ln[1 - \exp(-E_g/k_B T)], \tag{3}$$

as $T \to 0$ [cf. (1)]. The exchange parameter J is identified with the combination of J_1, J_2, and J_3 given above. In the least-squares fits of the data to Eq. (2) the quantities $f(0)$, C, and E_g have been taken as variables. $\mathcal{L}(T)$ has been calculated by use of the exact spin-wave expression, explained above. It should be noted that $\mathcal{L}(T)$ is slightly dependent on the value of J, the dependence being negligible at low temperatures [cf. Eq. (3)]. For the purpose of calculating $\mathcal{L}(T)$ we have therefore entered values of J, derived from the literature, which are 8.6°K for K_2MnF_4[5] and 112°K for K_2NiF_4.[3]

For K_2MnF_4, as no data are available on the temperature dependence of E_g, the fitting procedure was carried out assuming both $E_g \propto \langle S_z \rangle$ as for K_2NiF_4[14] and $E_g \propto \langle S_z \rangle^{3/2}$ as for MnF_2.[15] The latter assumption gave a somewhat better fit (although the variations in $f(0)$, C, and E_g are within the errors), and is adopted henceforth. The $f(T)$ data could be least-squares adjusted to the theory over the range $1.5°K \leq T \leq 25°K$. Inclusion of data for $T > 25°K$ gave rise to minor systematic deviations from the theory. The curve shown in Fig. 1 fits the data within experimental scatter for $1.5 \leq T \leq 25°K$ and corresponds to $f(0) = 150.476 \pm 0.003$ MHz,[16] $C = (3.14 \pm 0.03) \times 10^{-3}$/°K, and $E_g(0)/k_B = 7.38 \pm 0.08°K$. The gap temperature obtained is in excellent agreement with the value $7.40 \pm 0.15°K$ obtained from Breed's[5] spin-flop measurements.

For K_2NiF_4, antiferromagnetic resonance (AFMR) experiments[14] have given the spin-wave gap energy $E_g(0)/k_B = 27.4 \pm 0.2°K$, and have shown that $E_g(T)$ varies essentially linearly with the sublattice magnetization. A fit to within experimental scatter was obtained up to 50°K (Fig. 1), with the results $f(0) = 155.423 \pm 0.003$ MHz,

$C=(1.80\pm0.02)\times10^{-3}/°K$, and $E_g(0)/k_B=28.15\pm0.2°K$. The disparity between $E_g(0)$ so determined and the AFMR value is just outside the error limits, and may be evidence for exchange coupling between next-nearest-neighbor planes. Such a coupling modifies the low-temperature expression, Eq. (3), for $\mathfrak{L}(T)$ to become

$$\mathfrak{L}(T)\simeq-\frac{T}{2\pi}\int_{-\pi}^{\pi}d\theta\ln\left\{1-\exp\left[-\frac{E_g(T)[1+\delta(1-\cos\theta)]^{1/2}}{k_BT}\right]\right\}, \tag{4}$$

where $\delta=|J_z/2\alpha J|$, and J_z is the exchange coupling assumed between corresponding ions (only) in second-neighbor planes. If $\delta\ll1$ as expected, the effect of J_z is to increase the gap energy in Eq. (3) to roughly $E_g(T)(1+\delta/2)$, whereas J_z changes the low temperature AFMR frequency only by an amount $\sim J_z/J\ll\delta$. The observed disparity gives $\delta\approx0.05$ and $|J_z/J|\approx2\times10^{-4}$, which is well below the limits of resolution of the neutron search[3] for interplanar coupling and is an order of magnitude larger than dipolar coupling between second-neighbor planes. In view of the errors we feel that this value of $|J_z|$ is best regarded as an upper limit. The corresponding upper limit for K_2MnF_4 is $|J_z/J|\approx4\times10^{-4}$. This is obtained from the error limits on the spin-flop determination of E_g and that given here.

The low-temperature portion of the data fit for K_2NiF_4 is shown to better advantage in Fig. 2, where $f(0)-f(T)$ is plotted against $\mathfrak{L}(T)$. In this plot $\mathfrak{L}(T)$ is given by Eq. (3) to within 0.5%. To contrast our results with typical three-dimensional spin-wave behavior, the experimental ^{19}F frequency data[17] for MnF_2 are plotted against $\mathfrak{L}(T)$, as approximated by Eq. (3), in Fig. 2 with $E_g(0)/k_B=12.5°K$.[15] A definite curvature is found.

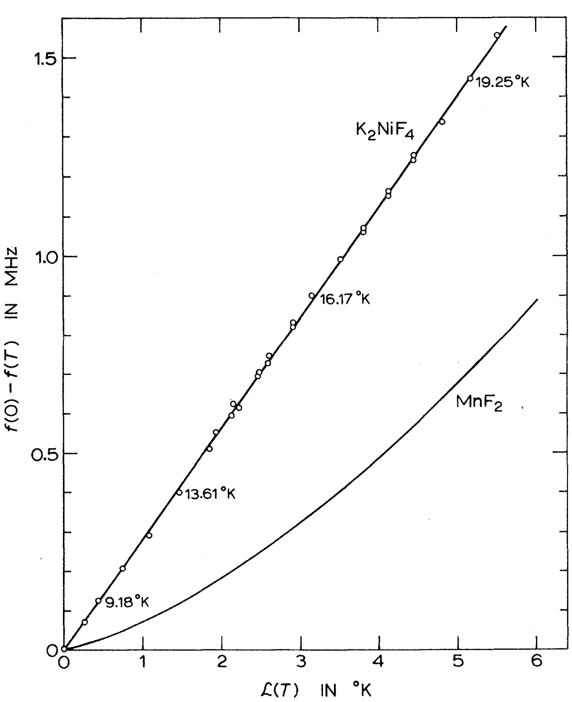

FIG. 2. The decrease of the resonance frequency $f(0)-f(T)$ for K_2NiF_4 versus the function $\mathfrak{L}(T)$ with the temperature as an implicit parameter. The straight line corresponds to the theoretical curve plotted in Fig. 1. The lower curve represents a similar plot of experimental data for MnF_2.

The usual procedure for evaluating the zero-temperature effective spin value $S-\Delta_0$ from NMR studies, combining $f(0)$ with the transferred hyperfine coupling coefficient as determined in the paramagnetic state, contains many uncertainties in the present case. Instead, we assume the validity of long-wavelength spin-wave theory as embodied in Eqs. (1)-(3) and derive the zero-point spin reduction Δ_0 from the value C obtained from the fit and literature values of the exchange constant. This is particularly favorable for K_2NiF_4, where the spin reduction is an appreciable fraction of $S=1$. For this compound neutron studies give $|J_1|[1-(J_2+2J_3)/J_1]=9.68\times10^{-3}$ eV $\pm$ 1%,[3] yielding

$$\Delta_0=0.21-0.79(J_2+2J_3)/J_1\pm0.03, \tag{5}$$

where terms of order $(J_2+2J_3)^2/J_1^2$ are neglected. Available measurements[7] suggest that $(J_2+2J_3)/J_1$ is of order 0.01. Thus we find $\Delta_0=0.20\pm0.03$, in better agreement with the spin-wave value $\Delta_0=0.18$ (including anisotropy effects)[18] than the perturbation theory value $\Delta_0\approx0.12$ (for $S=1$).[19]

[1]E. Legrande and R. Plumier, Phys. Status Solidi 2, 317 (1962).

[2]R. J. Birgeneau, H. J. Guggenheim, and G. Shirane, Phys. Rev. Letters 22, 720 (1969).

[3]J. Skalyo, G. Shirane, R. J. Birgeneau, and H. J. Guggenheim, Phys. Rev. Letters 23, 1394 (1969).

[4]This crystal is the same one used in the antiferromagnetic resonance experiments reported by R. J. Birgeneau, F. De Rosa, and H. J. Guggenheim, to be published.

[5]D. J. Breed, Physica 37, 35 (1967).

[6]G. K. Wertheim, H. J. Guggenheim, H. J. Levinstein, D. N. E. Buchanan, and R. C. Sherwood, Phys. Rev. 173, 614 (1968).

[7]Recent susceptibility studies of dilute $KMgF_3:Ni^{2+}$

and K_2MgF_4:Ni^{2+} [Y. Yamaguchi and N. Sakamoto, J. Phys. Soc. Japan 27, 1444 (1969)] give $J_1 \approx 110°K$, and $J_2/J_1 \approx 0.005$ for both cases. Effects of J_3 are presumably included in J_2. Other relevant results for the perovskites are $J_2/J_1 = 0.01$ in $KMgF_3$:Mn^{2+} [C. G. Windsor, thesis, Oxford University, 1963 (unpublished)]; $J_2/J_1 = 0.029$ in $KMnF_3$ [S. J. Pickart, M. F. Collins, and C. G. Windsor, J. Appl. Phys. 37, 1054 (1966)].

[8]We thank M. E. Lines of this laboratory for the use of his computer calculations for the quadratic layer antiferromagnet. We have made independent checks of these computations which agreed within round-off error.

[9]J. A. Eisele and F. Keffer, Phys. Rev. 96, 929 (1954).

[10]A. Brooks Harris, Phys. Rev. 143, 353 (1966).

[11]Yamaguchi and Sakamoto, Ref. 7.

[12]A phenomenological derivation of the fourth-order corrections has been given given by F. Keffer in Handbuch der Physik, edited by S. Flügge (Springer, Berlin, 1966), Vol. 18, Part II. In this formulation S is replaced with an effective spin value $S[1+0.079\,S^{-1}+l(T)]$, with $l(0)=0$. Calculating $l(T)$ to the same approximation as Eq. (1) gives $l(T_N/2) \approx -0.5\,\%$ for K_2MnF_4 and $l(T_N/2) \approx -0.1\,\%$ for K_2NiF_4. Thus the renormalization of S is essentially constant over the range of our data fits.

[14]Birgeneau, DeRosa, and Guggenheim, Ref. 4.

[15]F. M. Johnson and A. H. Nethercot, Phys. Rev. 104, 847 (1956), and 114, 705 (1959).

[16]For K_2MnF_4 we find $f\,(4.2°K) = 150.092 \pm 0.003$ MHz in reasonable agreement with the value 150.06 MHz reported by M. J. Rubinstein and V. J. Folen, Phys. Letters 28A, 108 (1968).

[17]V. Jaccarino and L. R. Walker, J. Phys. Radium 20, 341 (1959).

[18]M. E. Lines, to be published.

[19]L. R. Walker, unpublished calculation.

ASYMMETRIC SPIN-ORBIT EFFECTS CALCULATED FOR THE TOTAL REFLECTION OF POLARIZED COLD NEUTRONS

P. H. Handel
Department of Physics, University of Missouri—St. Louis, St. Louis, Missouri 63121
(Received 29 December 1969)

Strange asymmetries observed in magnetic neutron guides are explained in terms of an additional surface current due to the spin-orbit interaction of the neutrons in the Coulomb field of the atoms. This result enhances the approach of the index of refraction for the total reflection of neutrons using the propagator of the Schrödinger equation.

Within the framework of the theory of the index of refraction for neutrons[1] total reflection of neutrons is always symmetric. This means that the direction and the intensity of the totally reflected beam as well as the associated surface creep current do not depend on the sign of the scalar triple product $(\vec{\sigma}, \vec{n}, \vec{k})$ or $(\vec{\sigma}, \vec{k}, \vec{k}')$, where $\vec{\sigma}$ and $\vec{n}$ are the unit vectors of the polarization and of the external normal of the reflecting surface and $\vec{k}, \vec{k}'$ are the wave vectors of the incoming and totally reflected beam. A term proportional to $(\vec{\sigma}, \vec{k}, \vec{k}')$ in the scattering amplitude would not contribute to the index of refraction which depends only on the forward-scattering amplitude.

On the other hand, neutron guides[2] with ferromagnetic walls ($Fe_{0.5}$-$Co_{0.5}$ alloy, for instance) yield a significant and reproducible difference in the intensity and polarization of the outgoing neutrons,[3] according to whether they are bent to the right or to the left in the plane of $\vec{n}$ and $\vec{k}$. This new effect was observed by Berndorfer,[3] in a 5-m-long neutron guide of section 0.5×5.7 cm^2 bent circularly approximately 10^{-2} rad in the plane perpendicular to the magnetization. The change in intensity was a few percent, but the change in polarization was about 30 %.

The aim of this communication is to explain this effect, showing that a certain asymmetry of the surface creep current is obtained if the spin-orbit interaction is taken into account. The spin-orbit interaction V of neutrons with the Coulomb electric field of the scattering atoms is due to the magnetic field induced by the Coulomb field in the rest frame of the neutron[4,5]:

$$V = -1.91(\mu_N/mc)(\vec{\sigma}, \vec{E}, \vec{p}). \qquad (1)$$

Here $1.91\mu_N$ is the magnetic moment of the neutron, μ_N the nuclear magneton, m the neutron mass, $\vec{E}$ the electric field of a scattering atom, $\vec{\sigma}$ the Pauli spin operator, and $\vec{p}$ the momentum of the incoming neutron.

Considering V as a small correction in the Hamiltonian of the neutron, we use first-order perturbation theory in the propagator form. The unperturbed state ψ_0 in a total reflection experiment with $x^{(3)} = z = 0$ as mirror surface is[6]

$$\psi_0(\vec{x}, t) = (1 + e^{i\varphi})e^{i\vec{k}\cdot\vec{x} - \kappa z}, \quad z > 0, \qquad (2)$$

$$= e^{i\vec{k}\cdot\vec{x}} + e^{i\vec{k}'\cdot\vec{x} + i\varphi}, \quad z < 0, \qquad (3)$$