

Absolute Magnetic Moment of CoF₂ and NiF₂ from High-energy Magnetic X-ray Diffraction

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Introduction

With the development of the new synchrotron radiation sources, it has become possible to use magnetic x-ray scattering as a method of separating spin (S) and orbital (L) moment contributions directly. The ratio L/S can be determined with nonresonant magnetic scattering in the regime of conventional hard x-ray energies (4-20 keV) by using polarization analysis [1]. By combining these results with those from magnetic neutron diffraction, which measures the total magnetic moment, the spin magnetic moment can be extracted.

In contrast, high-energy magnetic x-ray diffraction is sensitive to the ordered spin component only; the spin magnetic moment is measured directly. When the magnetic signal is normalized to the charge signal, this value can be determined on an absolute scale with an accuracy of about 2%, as has been shown for FeF₂ [2]. This normalization technique is analogous to that of magnetic neutron diffraction, in which the absolute value of the total magnetic moment can be determined by normalizing the magnetic scattering to the nuclear signal. It turns out that for FeF₂, the measured spin magnetic moment is, within error, identical to the spin moment expected for the free magnetic ion [2].

The results of the work presented here on CoF₂ and NiF₂ agree with the values of the free ion for NiF₂ but differ considerably for CoF₂ [3]. In addition to determining the magnetic moment for NiF₂ and CoF₂, we have investigated the temperature dependence of the magnetic Bragg intensities.

Methods and Materials

Because of the low absorption of the high-energy photons in matter, it is possible to investigate the bulk properties of the same materials with neutrons and high-energy x-rays, even within the same sample environments. The differential scattering cross section for magnetic diffraction for high photon energies above 80 keV takes the following simple form [4]:

$$\frac{d\sigma}{d\Omega} = r_0^2 \left(\frac{\lambda_C}{d} \right)^2 |S_{\perp}|^2, \quad (1)$$

where r_0 is the classical electron radius, λ_C the Compton wavelength, d is the interplanar lattice spacing, and S_{\perp} is the Fourier transform of the spin

component perpendicular to the diffraction plane. For neutrons, on the other hand, the diffracted intensity is proportional to the linear combination $L(Q) + 2S(Q)$ of the Fourier transforms of the orbital and spin angular momenta. Thus, by combining the results of high-energy x-ray and neutron diffraction experiments, orbital and spin contributions can be separated without further theoretical assumptions.

CoF₂ and NiF₂ have the same tetragonal rutile-type crystal structure with space group P4₂/mnm; NiF₂ develops a small orthorhombic distortion below T_N [5]. At low temperatures, CoF₂ (as do MnF₂ and FeF₂) exhibits a two-sublattice antiferromagnetic ordering in which all spins are aligned along the tetragonal c-axis. In NiF₂, the moments lie in the ab-plane at an angle of about 0.9° to the b-axis, resulting in a small ferromagnetic moment along the a-axis [6, 7]. Because of the nonsymmorphic space group, the Bragg reflections of type ($h00$) and ($00l$) with h or l odd are extinct in all compounds, allowing the measurement of the weak magnetic reflections at these positions. The CoF₂ sample has a thickness of about 1.91 mm with a face of 2.3×2.2 mm² and a mosaicity of 6.8 ± 0.5 arcsec. The NiF₂ sample has dimensions of $1.5 \times 2.8 \times 3.3$ mm³ and a mosaicity of 8.5 ± 0.05 arcsec for the ($00l$) direction.

As sample environments, a He flow cryostat was used at the BESSRC sector beamline at the APS, and an Orange cryostat was used for the experiment at the MU-CAT sector beamline. Experiments were conducted in bisecting mode. In order to avoid the dominant Renninger reflections due to multiple scattering, ψ scans were performed while maintaining the reflecting condition. In the case of NiF₂, a 900-G magnetic field was applied along the beam direction (a*-axis). The ($00l$) direction was used as the scattering direction, thus leaving the ($h00$) direction perpendicular to the scattering plane.

Results

The temperature dependencies of the integrated intensities of the (300) and (001) reflections for CoF₂ and NiF₂ were measured from low temperatures up to the phase transition temperatures at beamline station 11-ID-C at the APS. Critical exponents were

determined to be $\beta = 0.306 \pm 0.006$ for CoF_2 and $\beta = 0.311 \pm 0.004$ for NiF_2 . The overall temperature dependency of the integrated intensity for CoF_2 shows a behavior close to that of an Ising magnet, whereas that for NiF_2 can be described by mean field theory.

The intensities of the magnetic (100) and (300) reflections of CoF_2 were measured at beamline station 11-ID-C at the lowest accessible temperature of 4.6K at a photon energy of 115 keV. The integrated intensities were determined with the c-axis perpendicular to the scattering plane. In addition, the (200) and (400) charge reflections were measured. These were used to normalize the magnetic reflections to obtain absolute magnetic moments according to the following equation:

$$|F_m|^2 = \frac{I_m}{I_c} \left(\frac{d}{\lambda_c} \right)^2 \frac{\sin 2\theta_m}{\sin 2\theta_c} |F_c|^2 \frac{y_{ext}}{W_m}. \quad (2)$$

Here, I_m and I_c are the integrated magnetic and charge intensities, θ_m and θ_c are the Bragg angles of the magnetic and charge reflections, F_c is the charge density structure factor, and W_m is the Debye-Waller factor of the magnetic reflection. The structure factors calculated from Eq. (2) are shown in Fig. 1.

In order to eliminate possible systematic errors due to absorption, extinction, or dead time of the counting chain, the experiment on CoF_2 was repeated at MU-CAT beamline station 6-ID-D at a photon energy of 150 keV. The (100) and (500) reflections were measured. The corresponding structure factors are shown in Fig. 1.

For NiF_2 , the magnetic (001) and (003) reflections were measured at beamline station 11-ID-C at ψ of ≈ 0 . The magnetic intensities were normalized to the charge intensities obtained from the (002) and (004) reflections. The structure factors for this compound are shown in Fig. 2.

The charge structure factors for both compounds, which are essential for the determination of the absolute magnetic intensities, have been determined very accurately by γ -ray experiments at a photon energy of 316.5 keV by using an ^{192}Ir -source [8]. Details about the different corrections applied to the charge intensities are given in Ref. 3.

The 150-keV experiment at the MU-CAT beamline confirmed the 115-keV BESSRC result, with reduced extinction. The spin magnetic moment was obtained from a fit of the free ion form factor $f(Q) = \langle j_0(Q) \rangle$ to the structure factor values. The magnetic moment is then obtained directly from $f(Q = 0)$. Both experiments give exactly the same result. We take $\mu_s = 2.213 \pm 0.012 \mu_B$ as our final value, uncorrected for the zero-point motion. This corresponds to $S = 1.107 \pm 0.009$. The resulting value if a correction of the zero point

motion of the moment of 2%, similar to FeF_2 [2], is applied, is $\mu_s = 2.258 \pm 0.015 \mu_B$. This value is 25% smaller than the value for the free Co^{2+} ion of $\mu_s = 3 \mu_B$.

For NiF_2 , the effect of the canting of the spins on the absolute value of the magnetic moment is negligible. The value of $\mu_s = 1.958 \pm 0.022 \mu_B$ is identical to the value of the magnetic moment of the free Ni^{2+} ion of $\mu = 2 \mu_B$ if a 2% reduction due to zero-point motion is considered.

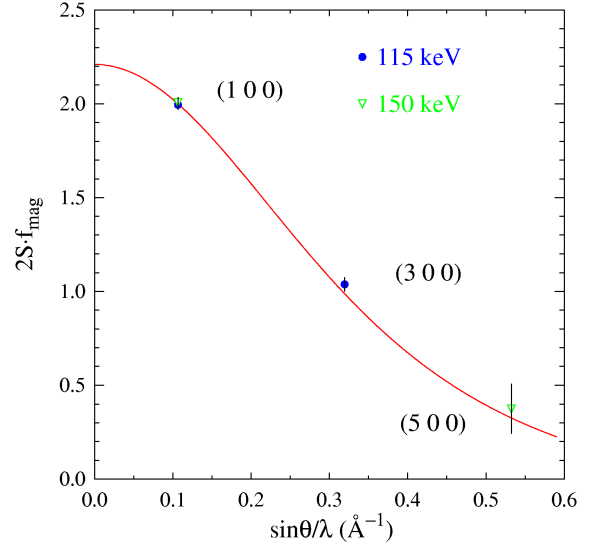


FIG. 1. Absolute magnetic structure factor of CoF_2 at $T = 5\text{K}$. The solid line shows a fit of $\langle j_0 \rangle$ for the free Co^{2+} ion to the data.

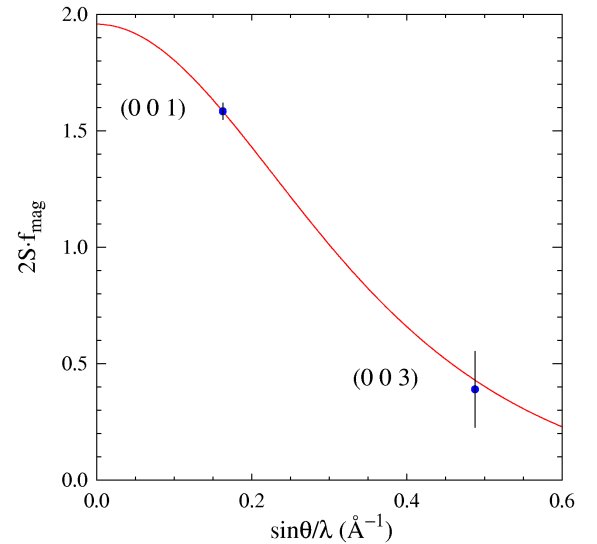


FIG. 2. Absolute magnetic structure factor of NiF_2 at $T = 10\text{K}$. The solid line shows a fit of $\langle j_0 \rangle$ for the free Ni^{2+} ion to the data.

Discussion

NiF₂ and CoF₂ show Ising-type behavior in the critical region. The critical exponent found for CoF₂ of $\beta = 0.306 \pm 0.006$ agrees very well with the result $\beta = 0.305 \pm 0.030$ obtained by Cowley and Carneiro [9], who fit the power law only in a region of a few millikelvin close to T_N . In our case, this exponent was found to be valid over a region between $0.7 T_N$ and T_N .

The data on the spin magnetic moment NiF₂ confirm the ionic character of this compound; the full free-ion moment is found just like for FeF₂. We cannot reproduce the results obtained by Brown, Figgis, and Reynolds [10, 11], who suggest a spin depolarization due to a covalent bond fraction of 28% between Ni and F from polarized neutron diffraction and *ab initio* calculations of spin densities in the local density approximation. Our results agree with those of Palmer and Jauch [8], who performed multipole refinement of γ -ray diffraction data at room temperature and at 15K and came to conclusions about the ionic character of this compound.

In contrast, the spin magnetic moment measured for CoF₂ is considerably reduced from the free-ion value. For the four compounds, the electronic charge density distributions have been studied by using highly accurate structure factors measured with 316.5-keV γ -radiation. In all cases, the total number of 3d electrons on the metal ion (i.e., the monopole population) turned out to be virtually identical with the formal integer values; for example, $P(3d) = 6.95 \pm 0.03$ e for CoF₂ [12]. The spin reduction on Co therefore cannot be related to charge transfer toward the ligands. Instead of charge transfer, a mixture of high-spin and low-spin configurations in the 3d orbitals may occur in CoF₂, which could lead to a considerable reduction of the magnetic moment. Molecular field calculations by Lines [13] give an effective spin S of 1.09, which is reduced to a value of 1.06 by spin waves. Our findings strongly support this result. In this theory, only spin operators that describe the two lowest molecular field states have been included, but this already seems to describe our data very well.

When the temperature dependency of the sublattice magnetization in CoF₂ is compared to the temperature dependencies of MnF₂, FeF₂, and NiF₂, it becomes clear that anisotropy (i.e., a nonquenched orbital contribution), is significant for CoF₂ and leads to more rapid saturation. Unlike the case for MnF₂, in which the anisotropy field acting on the Mn²⁺ ion is much weaker than the exchange field, for CoF₂, the opposite is true.

Therefore, a totally different magnetic behavior and a reduction of the spin magnetic moment are quite possible. The CoF₂ g-factor of 2.60 calculated by Khan et al. [14] clearly shows the considerable contribution of an orbital moment to the total magnetization. It is larger than the corresponding values for the other three compounds.

Acknowledgments

Synchrotron work was performed at the BESSRC (sector 11) and MU-CAT beamlines at the APS. This work has been supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES), Division of Materials Sciences, under Contract No. W-31-109-ENG-38 and the State of Illinois under the Higher Education Cooperation Act (HECA). The MU-CAT sector at the APS is supported by DOE BES through the Ames Laboratory under Contract No. W-7405-ENG-82. Use of the APS was supported by DOE BES under Contract No. W-31-109-ENG-38.

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