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# Anomalous hyperfine interaction in $\text{CoF}_2$ investigated by high resolution neutron spectroscopy

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## Abstract

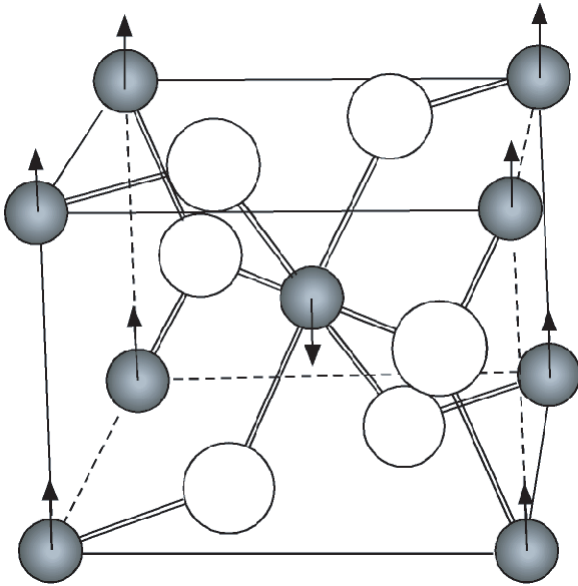
We investigated the low energy excitations in  $\text{CoF}_2$  in the  $\mu\text{eV}$  range with a back-scattering neutron spectrometer. The energy scans on a  $\text{CoF}_2$  powder sample revealed inelastic peaks at  $E = 0.728 \pm 0.008 \mu\text{eV}$  at  $T = 3.46 \text{ K}$  on both energy gain and energy loss sides. The inelastic peaks move gradually towards lower energy with increasing temperature and finally merge with the elastic peak at the electronic magnetic ordering temperature  $T_N \approx 37 \text{ K}$ . We interpret the inelastic peaks to be due to the transition between the hyperfine-split nuclear level of the  $^{59}\text{Co}$  isotopes with spin  $I = 7/2$ . We have shown that the energy of the inelastic peak or the hyperfine splitting in  $\text{CoF}_2$  can be treated as an order parameter of the antiferromagnetic phase transition and yields the critical exponent  $\beta = 0.313 \pm 0.007$ , consistent with the neutron diffraction results and also the three-dimensional Ising character of the magnetic system. The determined hyperfine splitting in  $\text{CoF}_2$  deviates from the linear relationship between the ordered electronic magnetic moment and the hyperfine splitting in Co, Co-P amorphous alloys and CoO, presumably due to the presence of an unquenched orbital moment.

(Some figures in this article are in colour only in the electronic version)

The method of determining the hyperfine splitting of the nuclear levels by spin-flip scattering of neutrons is now well established [1–17]. The relevant neutron scattering process can be summarized as follows: if neutrons with spin  $s$  are scattered from nuclei with spins  $I$ , the probability that their spins will be flipped is  $2/3$ . The nucleus, at which the neutron is scattered with a spin-flip, changes its magnetic quantum number  $M$  to  $M \pm 1$  due to the conservation of the angular momentum. If the nuclear ground state is split up into different energy levels  $E_M$  due to the hyperfine magnetic field or an electric quadrupole interaction, then the neutron spin-flip produces a change of the ground state energy  $\Delta E = E_M - E_{M \pm 1}$ . This energy change is transferred to the scattered neutron. If there is only one isotope then one expects a central elastic peak and two inelastic peaks of approximately equal intensities. The element Co is such a case because the isotope  $^{59}\text{Co}$  has 100% natural abundance and therefore the isotope incoherent scattering cross section is zero. The  $^{59}\text{Co}$  isotope has nuclear spin  $I = 7/2$  and its incoherent scattering cross section [18] is relatively large,

$4.8 \pm 0.3b$ . Therefore Co and Co-based compounds are suitable for studies of nuclear spin excitations. In fact Heidemann *et al* [4, 5] studied nuclear spin excitations in ferromagnetic Co and Co-P amorphous alloys and also the Co-based intermetallic compounds  $\text{LaCo}_{13}$ ,  $\text{LaCo}_5$ ,  $\text{YCo}_5$  and  $\text{ThCo}_5$ . Also Chatterji and Schneider [16] have recently investigated the low energy nuclear spin excitations in the transition metal oxide CoO. During the present investigation we studied low energy nuclear spin excitations in antiferromagnetic  $\text{CoF}_2$ .

$\text{CoF}_2$  belongs to the family of transition metal difluorides, which have been the subject of intensive investigations.  $\text{CoF}_2$  along with other transition metal difluorides  $\text{MnF}_2$ ,  $\text{FeF}_2$  and  $\text{NiF}_2$ , crystallize with the tetragonal rutile-type structure in the  $P4_2/mnm$  space group. However the magnetic properties of  $\text{CoF}_2$  are more complex than those of isomorphous  $\text{MnF}_2$ , because the Co ion has an unpaired angular momentum that plays an important role in determining its magnetic properties.  $\text{CoF}_2$  orders [19–23] below  $T_N \approx 37 \text{ K}$  with an antiferromagnetic structure (figure 1) with the propagation



**Figure 1.** The antiferromagnetic structure adopted by 3d transition metal difluorides, namely  $\text{CoF}_2$ , with the rutile-type crystal structure. The black circles represent the transition metal ion and the white circles represent the F ions. The arrows on the black circles represent the moment direction of the transition metal ions below the Néel temperature [24].

vector  $\mathbf{k} = 0$ . The Co ions at the corner (000) positions of the tetragonal unit cell are all parallel to the  $c$ -axis whereas the Co atom at the  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  positions are oppositely oriented. From NMR measurements Jaccarino [25] reported that the electronic magnetic moment of the Co ion in  $\text{CoF}_2$  produces, at the  $^{59}\text{Co}$  nucleus, a hyperfine field of approximately 18 T that yields a hyperfine splitting of 8.7 mK or  $0.75 \mu\text{eV}$ . At very low temperature ( $T < 20$  mK) Steiner *et al* [26] reported that Co nuclei become polarized, as evidenced by the appearance of the 001 reflection.

The presence of an orbital moment in  $\text{CoF}_2$  makes it particularly interesting for the study of the hyperfine interaction in this compound. It is interesting to investigate experimentally the effect of orbital moment on the hyperfine splitting and compare it with the results of *ab initio* calculations. Unfortunately such calculations have not yet been done on  $\text{CoF}_2$ , probably due to the absence of experimental data to compare with. The present experimental investigation of the hyperfine interaction in  $\text{CoF}_2$  may induce such calculations. Another important question is whether the energy of the nuclear spin excitations is proportional to the sublattice magnetization or the order parameter of the antiferromagnetic phase transition in  $\text{CoF}_2$ , and also in general. The proportionality of the hyperfine field and the magnetization have been assumed, often without justification and also often incorrectly [27]. We therefore decided to settle this question by measuring experimentally the temperature dependence of the energy of nuclear spin excitations with small enough temperature intervals, especially close to  $T_N$ , and to determine the critical exponent  $\beta$  and compare the result with those determined by neutron diffraction.

We performed inelastic neutron scattering experiments on  $\text{CoF}_2$  powder samples by using the high resolution back-scattering neutron spectrometer SPHERES [28] of the Jülich Centre for Neutron Science located at the FRMII reactor in Munich. The wavelength of the incident neutrons was  $\lambda = 6.271 \text{ \AA}$ . About 8 g of powder  $\text{CoF}_2$  sample was sealed in a He atmosphere inside a cylindrical Al sample holder which was fixed on the cold tip of a top-loading closed-cycle cryostat. We observed inelastic signals in  $\text{CoF}_2$  at energies  $E = 0.728 \pm 0.008 \mu\text{eV}$  on both energy gain and loss sides at  $T = 3.5 \text{ K}$ . The energy of the inelastic signal decreases continuously as the temperature is increased and finally merges with the central elastic peak at  $T_N \approx 37 \text{ K}$ . Figure 2 shows typical energy spectra of  $\text{CoF}_2$  at several temperatures. We examined the individual spectra from all the detectors placed at different  $Q$ -values and found no  $Q$ -dependence. The  $Q$ -dependence of the spectra is also not expected, at least in the temperature range we measured them. At very low temperatures one expects nuclear spin waves that should have a dispersion at a very small  $Q$ , of the order of  $0.01 \text{ \AA}^{-1}$  or less. The  $Q$  resolution of the back-scattering neutron spectrometers is much worse than this value and therefore it is not possible to measure nuclear spin wave dispersion with them. The spectra shown in figure 2 are the results of summing up the counts of the individual detectors placed at different scattering angles. The inelastic signals have resolution limited widths at least at low temperatures. The inelastic peaks move towards the central elastic peak as the temperature is increased, and at the ordering temperature they just merge with the central elastic peak thereby causing an increase in intensity of the elastic peak. We fitted the two inelastic and the central elastic peaks with Gaussian functions. The shape of the elastic peak at  $E = 0$  at low temperature is essentially determined by the resolution function of the back-scattering spectrometer. The resolution function was found to be asymmetric with a shoulder on the positive energy side. So the Gaussian function can describe the resolution function only approximately. We attribute the asymmetric shape due to the deviation from the perfect back-scattering geometrical situation. The asymmetric line shape hindered us from getting a good determination of the position, intensity and width of the inelastic peaks, especially the one at the positive energy side close to the ordering temperature at which the inelastic peak is very close to the central elastic peak. We interpret the inelastic signal observed in  $\text{CoF}_2$  due to the excitations of the  $^{59}\text{Co}$  nuclear spins  $I = \frac{7}{2}$ . In a first approximation one can consider these inelastic peaks to arise due to the transitions between the hyperfine-field-split nuclear levels.

The intensity of the inelastic peak at  $T = 3.5 \text{ K}$  is about one third of that of the elastic peak. One expects the peaks to be of equal intensities. Natural Co has only one isotope and therefore gives no isotope incoherent scattering. The incoherent scattering cross section of F is only  $0.0008 \pm 0.0002b$  and therefore does not contribute significantly to the intensity of the incoherent elastic peak. The remaining possibilities are the contributions from the sample holder and coherent Bragg peaks. The sample holder consists of Al which has a very small incoherent scattering cross section of  $0.0092 \pm 0.0007b$ . To decrease the background we used

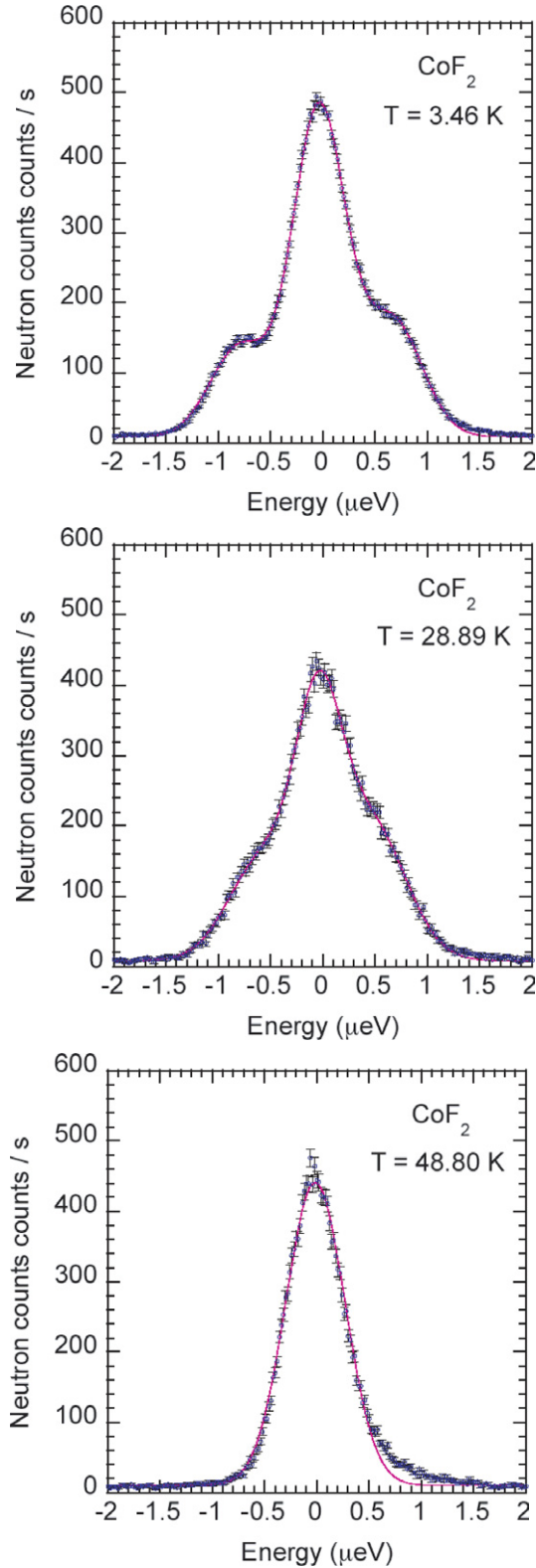


Figure 2. Typical energy spectra of CoF<sub>2</sub> at several temperatures.

Cd, which has a large incoherent scattering cross section of  $2.4 \pm 0.7b$ . These are the possible origins of the excess intensity in the elastic peak. Heidemann *et al* [2, 3, 6] observed a similar excess intensity at the elastic peak in several experiments on vanadium oxides.

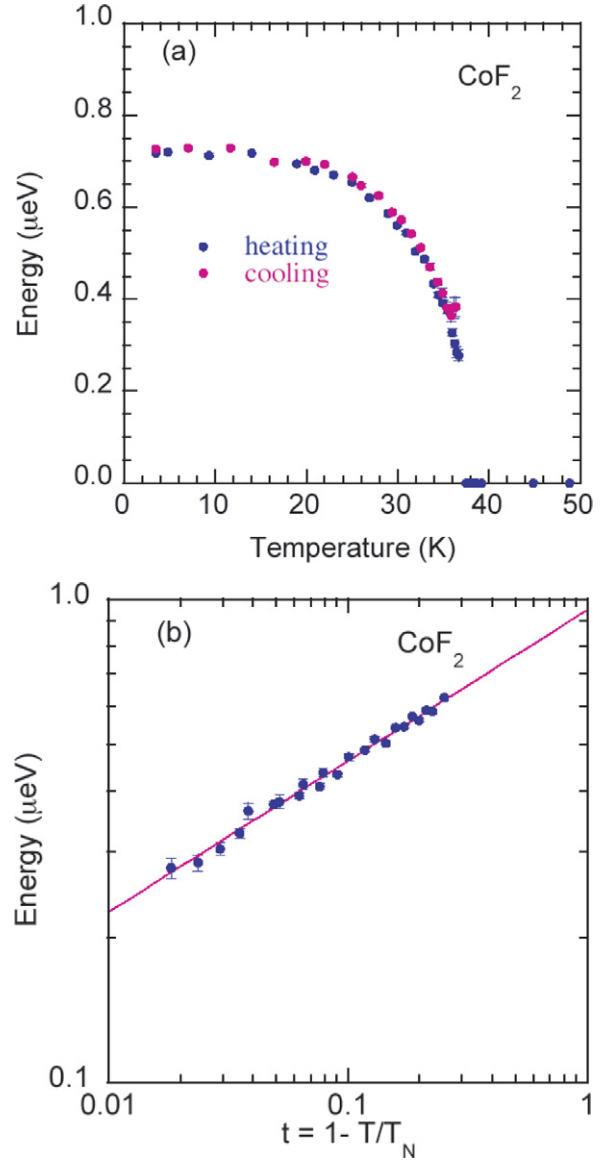


Figure 3. (a) Temperature variation of the energy of the inelastic peak of CoF<sub>2</sub>. (b) Log-log plot of the energy of the inelastic peak versus reduced temperature  $t = (T_N - T)/T_N$  that yields the critical exponent  $\beta = 0.313 \pm 0.007$ .

Figure 3(a) shows the temperature variation of the energy of the inelastic peak of CoF<sub>2</sub> both in the heating and in the cooling cycles. The absence of any appreciable hysteresis, and also the continuous variation of the energy as a function of temperature, shows that the antiferromagnetic phase transition in CoF<sub>2</sub> is of the second order. We checked whether the energy of the inelastic peak or the hyperfine splitting can be considered to be the order parameter of the phase transition. We therefore attempted to determine the critical exponent  $\beta$ , assuming the validity of the proportionality of the energy of inelastic peak with the sublattice magnetization of CoF<sub>2</sub>. The least squares fit of the data close to the Néel temperature to the power law

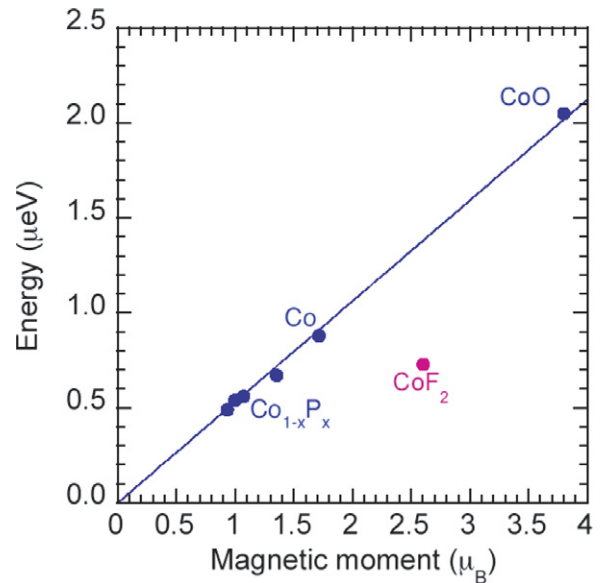
$$E(T) = E(0) \left(1 - \frac{T}{T_N}\right)^\beta \quad (1)$$

**Table 1.** Ordered electronic moment of Co and the energy of Co nuclear spin excitations.

Compound	Moment ( $\mu_B$ )	$\Delta E$ ( $\mu eV$ )	Reference
CoF <sub>2</sub>	2.60(4)	0.728(8)	Present work
CoO	3.80(6)	2.05(1)	[16]
Co	1.71	0.88	[4]
Co <sub>0.873</sub> P <sub>0.127</sub>	1.35	0.67	[4]
Co <sub>0.837</sub> P <sub>0.161</sub>	1.0	0.54	[4]
Co <sub>0.827</sub> P <sub>0.173</sub>	1.07	0.56	[4]
Co <sub>0.82</sub> P <sub>0.18</sub>	0.93	0.49	[4]

gave  $T_N = 37.2 \pm 0.2$  K and  $\beta = 0.313 \pm 0.007$ . Figure 3(b) shows a log–log plot of the energy versus reduced temperature. The critical exponent determined,  $\beta = 0.313 \pm 0.007$ , is close to the three-dimensional Ising value,  $\beta = 0.326$ , and also agrees well with the value determined by neutron diffraction [21, 22]. The agreement is a bit surprising and is probably accidental because we did not have enough data points close to  $T_N$ . Although we measured the spectra at many temperatures close to  $T_N$ , the proximity of the inelastic peaks to the elastic peak made the determination of their energies impossible. We can however conclude that the identification of the energy of the inelastic peak with the order parameter of the antiferromagnetic phase transition in CoF<sub>2</sub> is most likely justified.

Table 1 gives the ordered electronic moment of CoF<sub>2</sub> and the energy of Co nuclear spin excitations of CoF<sub>2</sub> determined during the present investigations, along with the similar data obtained by Heidemann *et al* [4] in Co and Co–P amorphous alloys and Chatterji *et al* [16] in CoO. Figure 4 shows a plot of the energy of inelastic peaks observed in CoF<sub>2</sub> along with that reported in CoO [16], Co and Co–P alloys [4] versus the corresponding saturated electronic magnetic moment of Co in these compounds. The data corresponding to all of these compounds, except for CoF<sub>2</sub>, lie approximately on a straight line showing that energy of the inelastic peak or the hyperfine splitting of the nuclear level is approximately proportional to the electronic magnetic moment. The slope of the linear fit of all data without that of CoF<sub>2</sub> gives a value of  $0.531 \pm 0.006 \mu eV/\mu_B$ . The present experimental results CoF<sub>2</sub> do not fit at all with the straight line. This is most likely related to the existence of different orbital moments of Co ions in different compounds. The orbital magnetic moment in CoF<sub>2</sub> is not known with certainty. Jauch *et al* [23] determined the total ordered magnetic moment of the Co ion in CoF<sub>2</sub> to be  $2.60 \pm 0.04 \mu_B$  from their neutron powder diffraction investigation. Stempfner *et al* [22] determined the spin magnetic moment of Co in CoF<sub>2</sub> to be  $\mu_S = 2.21 \pm 0.02 \mu_B$  from their high energy x-ray magnetic diffraction investigation. Assuming collinearity, the orbital magnetic moment is  $\mu_L = 0.4 \mu_B$ . The orbital moment in Co is known to produce a hyperfine field that has the opposite sign to that generated by the spin moment [5, 27]. So the orbital moment in CoF<sub>2</sub> may be the cause of the reduction of the hyperfine field compared to that in CoO, Co and Co–P amorphous alloys and hence the deviation from the linear relationship. Such a reduction in hyperfine fields and deviation from linear relationship has also been observed by Heidemann *et al* [5] in

**Figure 4.** Plot of the energy of the inelastic signal versus the ordered electronic moment of Co-based materials.

the intermetallic compounds LaCo<sub>5</sub>, YCo<sub>5</sub> and ThCo<sub>5</sub>, which also possess considerable orbital moments as determined by polarized neutron diffraction [29, 30].

In conclusion we have investigated the low energy excitations in CoF<sub>2</sub> by inelastic neutron scattering with a back-scattering neutron spectrometer. The present results, together with the results on Co and Co–P amorphous alloys studied by Heidemann *et al* [4, 5], have shown that the hyperfine field in CoF<sub>2</sub> is significantly smaller than that expected from the ordered magnetic moment of  $2.60 \mu_B$ . This is most likely related to the presence of a significant unquenched orbital moment of Co in CoF<sub>2</sub>.

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