Hyperfine interaction in Co_2SiO_4 investigated by high resolution neutron spectroscopy

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ABSTRACT

We have investigated the hyperfine interaction in Co_2SiO_4 by inelastic neutron scattering with a high resolution back-scattering neutron spectrometer. The energy spectrum measured from a Co_2SiO_4 powder sample revealed inelastic peaks at $E = 1.387 \pm 0.006\,\mu eV$ at $T = 3.5\,K$ 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 $T_N \approx 50\,K$. The inelastic peaks have been interpreted to be due to the transition between hyperfine-split nuclear level of the ^{59}Co isotopes with spin $I = \frac{7}{2}$. The temperature dependence of the energy of the inelastic peak in Co_2SiO_4 showed that this energy can be considered to be the order parameter of the antiferromagnetic phase transition. The determined hyperfine splitting in Co_2SiO_4 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 unquenched orbital moment. These results are very similar to those of CoF_2 recently reported by Chatterji and Schneider [7].

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Hyperfine interactions have been studied for many years and by different methods [1]. The techniques for studying hyperfine interactions in magnetic materials, such as nuclear orientation and nuclear specific heats, the Mössbauer effect, nuclear magnetic resonance, angular correlation of $\gamma-$rays interaction of polarised neutrons with polarised nuclei, provided improved understanding of the electronic magnetism and also nuclear magnetism at the same time. Another less well-known method is to determine the hyperfine splitting of the nuclear levels directly by spin–flip scattering of neutrons [2]. 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}Co has 100% natural abundance and therefore the isotope incoherent scattering cross-section is zero. The ^{59}Co isotope has nuclear spin $I = \frac{7}{2}$ and its incoherent scattering cross-section [3] is relatively large, 4.8 ± 0.3 b. Therefore Co and Co-based compounds are suitable for the 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 Co-based intermetallic compounds $LaCo_{13}$, $LaCo_5$, YCo_5 and $ThCo_5$. Also Chatterji and Schneider [6,7] have investigated recently the low energy nuclear spin excitations in transition metal oxide CoO and transition metal difluoride CoF_2. During the present investigation we studied low energy nuclear spin excitations in antiferromagnetic Co_2SiO_4.

Co_2SiO_4 belongs to an important class of compounds with olivine-type crystal structure [8] that constitutes a major component of terrestrial crust. Co_2SiO_4 crystallizes in the orthorhombic space group *Pnma*. There are two crystallographic non-equivalent Co^{2+} sites, namely, Co1 (Wyckoff position 4a) with inversion symmetry $\bar{1}$, and Co2 (Wyckoff position 4c) with mirror symmetry *m*. At room temperature the lattice parameters are $a = 10.3005(1)\,Å$, $b = 6.0028(1)\,Å$ and $c = 4.7816(1)\,Å$. The Co1 cations is coordinated by six O ions forming $Co1O_6$ octahedra that are interconnected by common edges and form single chains along *b*. The Co2 cations also form $Co2O_6$ octahedra that are attached on alternate sides to the $Co1O_6$ chains in a way that the whole arrangement of $Co1O_6$ and $Co2O_6$ octahedra form zigzag

chains along the b axis. The Si cations are coordinated by four O ions forming SiO_4 tetrahedra that are linked to the $Co1O_6$ and $Co2O_6$ octahedra. Below $T_N \approx 50\,K$ Co_2SiO_4 orders to an anti-ferromagnetic structure [9–13] with a propagation vector $\mathbf{k} = (0,0,0)$ shown schematically in Fig. 1.

We investigated previously low energy nuclear spin excitations in several Nd-based compounds [14–20] and established that the energy of the excitations is linearly proportional to the magnetic moment of Nd ions. We wished to check whether a similar relationship exists also for Co-compounds. The Fe-group transition metal ions have more extended d electrons compared to the localized 4f electrons of the rare earth ions, which are well shielded. After finding anomalous hyperfine interaction [7] in CoF_2 that was known to have unquenched orbital moment we deliberately selected another Co-based compound Co_2SiO_4 for similar study because it also has substantial unquenched orbital moment [13]. Magnetic susceptibility and unpolarised neutron diffraction measurements [13] indicate the presence of important orbital contribution to the total magnetic moment of Co^{2+} in Co_2SiO_4. X-ray magnetic circular dichroism (XMCD) and polarised neutron diffraction measurements [13] give an orbital to spin magnetic moment ration $\mu_L/\mu_S \approx 0.25$. It is interesting to investigate experimentally the effect of orbital moment on the hyperfine splitting and compare with the results of ab-initio calculations. Unfortunately such calculations have not yet been done on Co_2SiO_4 probably due to the absence of experimental data to compare with. To our knowledge no NMR or Mössbauer study of the hyperfine interaction has been undertaken in Co_2SiO_4. The present experimental investigation of the hyperfine interaction in Co_2SiO_4 may induce some ab-initio calculations of the hyperfine interaction in Co_2SiO_4. Another important question is whether the energy of the nuclear spin excitations is proportional to the sublattice magnetisation or the order para-meter of the antiferromagnetic phase transition in Co_2SiO_4 and also whether this is also true for any magnetic phase transition in general. The proportionality of the hyperfine field and the magnetisation have been assumed often without justification and also often incorrectly [1]. We therefore decided to settle this question by measuring experimentally the temperature depen-dence of the energy of nuclear spin excitations with small enough temperature intervals especially close to T_N and determine the critical exponent β and compare the result with those determined by neutron diffraction. Chatterji and Schneider [7] have recently shown that the energy of the nuclear spin excitation or the hyperfine splitting can indeed be considered as the order parameter of the antiferromagnetic phase transition in CoF_2. To check whether this result is also valid in Co_2SiO_4 we investigated hyperfine interaction in this compound containing Co^{2+} ions with unquenched orbital moments.

We did inelastic neutron scattering experiments on Co_2SiO_4 powder samples by using the high resolution back-scattering neutron spectrometer SPHERES [21] of the Jülich Centre for Neutron Science located at the FRMII reactor in Munich. The wavelength of the incident neutron was $\lambda = 6.271\,\text{Å}$. About 3 g of powder Co_2SiO_4 sample was placed inside a flat Al sample holder which was fixed on the cold tip of a top-loading closed-cycle cryostat. We observed inelastic signals Co_2SiO_4 at energies $E = 1.387 \pm 0.006\,\mu eV$ at $T = 3.5\,K$ on both energy gain and loss sides. The energy of the inelastic signal decreases continuously as the temperature is increased and finally merges with the central elastic peak at $T_N \approx 50\,K$. Fig. 2 shows the typical energy spectra of Co_2SiO_4 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. The spectra shown in Fig. 2 are the results of summing up
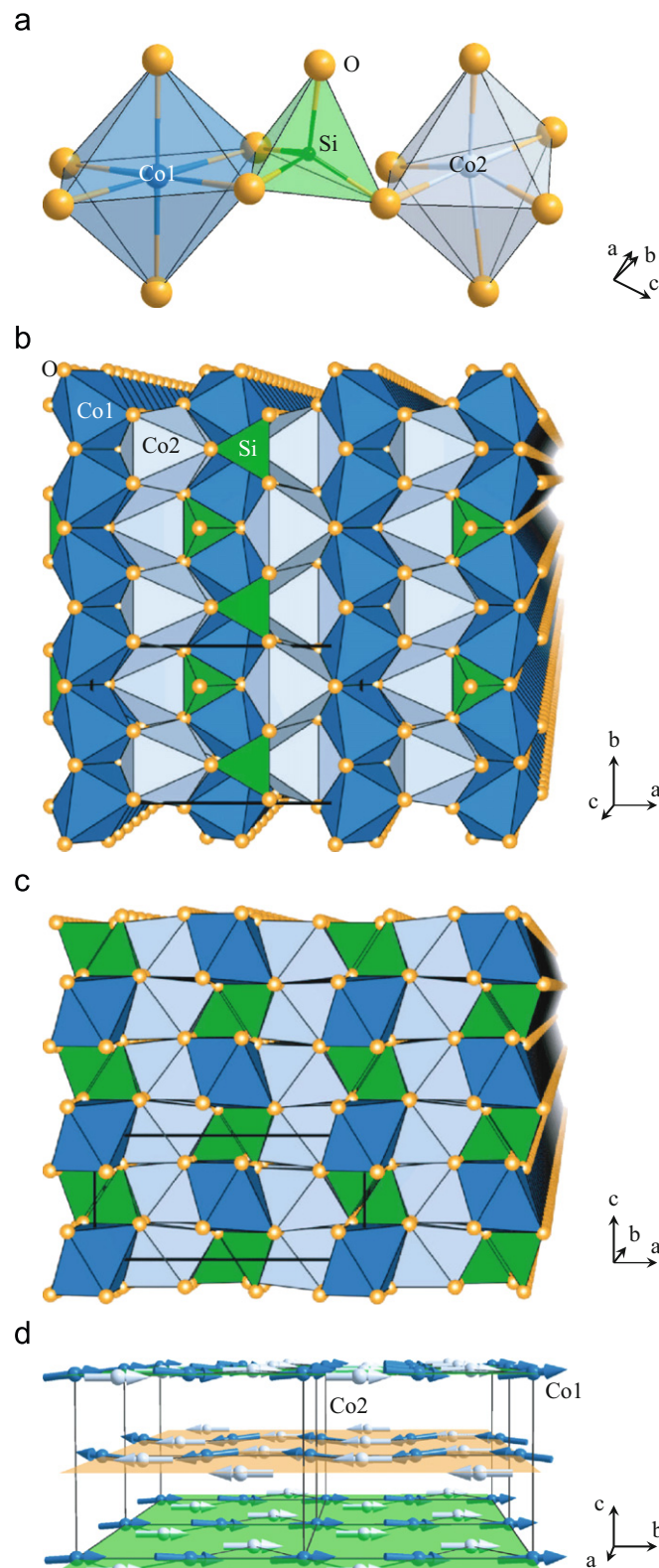
Fig. 1. (Color online) (a) Clinographic view of the CoO_6 and SiO_4 polyhedra in Co_2SiO_4. (b,c) Graphical representation of the crystal structure of Co_2SiO_4. (d) Graphical representation of the Co_2SiO_4 magnetic structure below 50 K. The non-magnetic atoms (Si and O) were excluded for simplicity.

the counts of the individual detectors placed at different scattering angles. We fitted the two inelastic and the central elastic peaks with Gaussian functions. The shape of the elastic