Direct observation of low energy nuclear spin excitations in HoCrO$_3$ by high resolution neutron spectroscopy

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Abstract

We have investigated low energy nuclear spin excitations in the strongly correlated electron compound HoCrO$_3$. We observe clear inelastic peaks at $E = 22.18 \pm 0.04$ $\mu$eV in both energy loss and gain sides. The energy of the inelastic peaks remains constant in the temperature range 1.5–40 K at which they are observed. The intensity of the inelastic peak increases at first with increasing temperature and then decreases at higher temperatures. The temperature dependence of the energy and intensity of the inelastic peaks is very unusual compared to that observed in other Nd, Co, V and also simple Ho compounds. Huge quasielastic scattering appears at higher temperatures presumably due to the fluctuating electronic moments of the Ho ions that get increasingly disordered at higher temperatures. The strong quasielastic scattering may also originate in the first Ho crystal-field excitations at about 1.5 meV.

(Some figures may appear in colour only in the online journal)

The coupling of the nuclear spin system with the electronic spin system through hyperfine interaction in condensed matter had been known for a rather long time. Recently this phenomenon has attracted renewed interest due to its possible application in spintronics and quantum computation [1, 2].

The principle of the method of studying the hyperfine interaction by using inelastic neutron scattering is well known [3, 4] and will not be repeated. This method can be used to study the magnetic ordering by measuring the hyperfine splitting of the nuclear levels for magnetic materials that contain magnetic atoms with non-zero nuclear spins and also having large spin dependent neutron scattering cross-sections.

In the past the high resolution inelastic neutron scattering technique has been used to study hyperfine interaction in V, Co, and Nd compounds [4–14] because of their relatively large spin dependent scattering cross-sections. Recently the Ho compounds have also become subjects of such studies. Ho compounds are also good candidates for such study since Ho has only one single stable isotope, $^{165}$Ho with a nuclear spin $I = 7/2$ and large magnetic dipole moment [15] of 4.17 $\mu N$. The neutron incoherent scattering cross-section [16] of $^{165}$Ho is 0.36 $\pm$ 0.03 b. Ehlers et al [17] observed recently nuclear spin excitations in Ho pyrochlore compound Ho$_2$Ti$_2$O$_7$. We also studied recently [18, 19] the low energy nuclear spin excitations in pure Ho and also the intermetallic HoAl$_2$. The temperature dependences of the energy and intensity of low energy nuclear spin excitations in Ho and HoAl$_2$ behave very similarly to those of Nd, Co and V compounds. The temperature dependence of the energy of nuclear spin excitations follows the order parameter of the magnetic phase transition, i.e., the energy decreases and becomes zero at the phase transition. This is not the case with Ho$_2$Ti$_2$O$_7$, which shows spin-ice behavior due to the magnetic frustration on the pyrochlore lattice. Here we report the results for another unusual strongly correlated electron compound HoCrO$_3$ that also behaves anomalously in this respect probably due to the presence of two magnetic sublattices of Ho and Cr and their interaction with each other.

HoCrO$_3$ crystallizes with the orthorhombically distorted perovskite structure in the space group $D_{2h}^{28}$-$Pbnm$ and has four formula units per unit cell. The magnetic properties...
of HoCrO$_3$ have been studied using magnetization and neutron diffraction in the second half of the last century. The exchange coupling between nearest-neighbor Cr$^{3+}$ ions is predominantly antiferromagnetic and these ions order magnetically [20–22] below $T_N \approx 142$ K. Below this temperature HoCrO$_3$ exhibits a weak ferromagnetic moment [22]. The magnetic structure of the Cr sublattice [22] is $G_F$, in the notation of Köhler et al [23] and Bertaut [24]. At lower temperature Ho ions order and due to strong interaction between Cr and Ho moments spin reorientation phenomena take place [25, 26]. The recent interest [27–31] in HoCrO$_3$ and other rare-earth chromites is due to the possibility of coupling between the magnetic and ferroelectric properties leading to multiferroic behavior and potential device applications.

Polycrystalline HoCrO$_3$ samples were synthesized by the solid state reaction of Ho$_2$O$_3$(3N) and Cr$_2$O$_3$(4N) in stoichiometric ratio [26]. The precursors were mixed intimately and subsequently heat treated at 1100°C for 48 h. The resulting material was then reground and annealed again at 1200°C for 24 h. The phase purity of the synthesized powder sample was then confirmed by means of powder x-ray diffraction with Cu Kα ($\lambda = 1.54059$ Å) radiation, using a Huber x-ray diffractometer (Huber G670) in transmission Guinier geometry. Specific heat, magnetization and also neutron diffraction measurements showed that the sample orders below $T_N \approx 142$ K.

Inelastic neutron scattering measurements were carried out on the BASIS back-scattering spectrometer [32] of the spallation neutron source (SNS) of the Oak Ridge National Laboratory in USA. The spectrometer utilizes inverted scattering geometry. The final energy of the neutrons scattered by the sample, $E_i$, is selected by the Si(311) analyzer crystals, that Bragg reflects neutrons with wavelength of 6.267 Å. The incident energy of the neutrons was centered on this wavelength with 0.5 Å bandwidth. The energy resolution of the spectrometer at the elastic peak is about 3.5 µeV. 5.2 g of powder HoCrO$_3$ sample was first evenly distributed inside an Al foil and then placed inside the annular space of a cylindrical double-wall Al sample holder. The sample holder filled with HoCrO$_3$ was placed inside a standard 4He cryostat and measurements were performed at different temperatures. For determining the resolution function of the spectrometer we also placed a vanadium standard sample inside the cryostat and made measurements on it under the same conditions.

We checked carefully for any significant $Q$ (momentum transfer) dependence of the measured inelastic spectra of HoCrO$_3$ and found none. This is in agreement with the results of previous investigations of hyperfine interactions in other materials. We therefore integrated the data over the measured $Q$ range which was about 0.4–1.8 Å$^{-1}$. Figure 1 shows the $Q$-integrated inelastic neutron scattering spectra of HoCrO$_3$ at several temperatures. At $T = 1.5$ K two clear inelastic signals are observed on both energy gain and loss sides. The average energy of these inelastic signals is at $E = 22.18 \pm 0.04$ µeV which is very close to the hyperfine splitting 20.68 µeV determined from the low temperature specific heat data [26]. We interpret these inelastic peaks to be due to the transition of the hyperfine-split nuclear levels. This energy is also very close to the energy (26.3 µeV) observed by Ehlers et al [17] in the Ho pyrochlore compound Ho$_2$Ti$_2$O$_7$.

We have fitted the spectra with the equation

$$S(\omega) = \left[ x\delta_{el}(\omega) + p_1\delta_{ins}(\omega) + p_2\delta_{ins}(\omega) \right] \otimes R(\omega) + B$$

(1)

where delta functions $\delta_{el}$ and $\delta_{ins}$ represent elastic and inelastic peaks respectively. The Lorentzian function $L$ represents the quasielastic component. The above mentioned terms are all convoluted numerically with the experimentally determined resolution function, $R(\omega)$, to conserve the asymmetric shape. $B$ is the flat background term and $x, p_1, p_2, p_3$ are scaling factors. The delta functions for the elastic peak and the two inelastic peaks when convoluted with the experimentally determined instrumental resolution function reproduce these three peaks quite well. This is also justified because these peaks are expected to have very small intrinsic broadening compared to the instrumental resolution function. We have also included the Lorentzian function to take into account any quasielastic scattering that may still exist at low temperatures. We will note later that increasingly strong quasielastic scattering does arise at higher temperatures. Figure 2 shows the fit of equation (1) to the measured data for several temperatures in the range 1.5–40 K. Figure 3 shows the temperature variation of the energy and intensity of the inelastic peak obtained from the least-squares fit. The energy of the inelastic peak remains almost constant in the temperature range 1.5–40 K and then becomes invisible. This temperature variation of the energy of the nuclear spin excitations is quite different from that of Nd, Co and also Ho compounds studied by us but is very similar to that for the Ho compound Ho$_2$Ti$_2$O$_7$ studied by Ehlers et al [17]. For Nd and Co compounds studied by us [5–14] the temperature dependence of the energy of the nuclear spin excitations follows the order parameter of the magnetic phase transition, i.e., the energy decreases and

![Figure 1. $Q$-integrated energy spectra of HoCrO$_3$ at several temperatures.](image-url)
Figure 2. Inelastic peaks of HoCrO$_3$ at $T = 1.5, 5, 10, 20, 30$ and $40$ K on both energy loss and gain sides fitted by convoluting the instrumental resolution function $R(\omega)$ determined from vanadium with one delta function $\delta_{el}$ for the elastic peak and with two delta functions $\delta_{ins}$ for the two inelastic peaks and a Lorentzian function $L$ for the quasielastic scattering. These components are shown by continuous curves of different colors indicated by the legends. The legends also indicate the kinds of functions (scaled and convoluted with the resolution function) of the components by using the symbols of equation (1). At $T = 1.5$ K it was not necessary to include the Lorentzian function for the fit because of the absence of quasielastic scattering at this temperature. At all other temperatures the Lorentzian function had to be included.

becomes zero at the phase transition. The inelastic peaks move towards the central elastic peak and merge with it at the magnetic phase transition. This was also the case for Ho metal [18] and the intermetallic compound HoAl$_2$ [19]. It is surprising that the energy of the inelastic peak does not follow the temperature dependence of the ordered magnetic moment of Ho ions deduced from neutron diffraction [26, 33]. The intensity of the inelastic peak increases a bit with temperature and then decreases continuously and becomes very small at about 40 K. At higher temperatures the inelastic signal disappears or becomes invisible probably due to the appearance of huge quasielastic scattering. This behavior is also very different from the intensity variation observed in the Nd, Co and other Ho compounds, but
Figure 3. Temperature variation of the energy and intensity of the inelastic peak of HoCrO$_3$. The least-squares error bars are smaller than the symbols or of about the same size. The continuous curves are just guides to the eye.

is again similar to that observed by Ehlers et al [17] in Ho$_2$Ti$_2$O$_7$.

Another interesting outcome of the present study is the discovery of huge quasielastic scattering at higher temperatures. Figure 4 shows the spectra of HoCrO$_3$ measured at 50, 60 and 100 K. At these temperatures the inelastic peaks due to hyperfine interaction are not observed. Strong quasielastic scattering dominates the spectra. We have fitted the spectra with the equation

$$S(\omega) = [x\delta(\omega) + p3L(\Gamma, \omega)] \otimes R(\omega) + B$$  (2)

where the second and the third terms within square brackets of the previous equation (1) representing the two inelastic peaks are deleted because of the absence of inelastic peaks at these temperatures. We are here left with the elastic peak $\delta_\omega$ and the Lorentzian $L(\Gamma, \omega)$ convoluted with the resolution function $R(\omega)$. $B$ is the background as in equation (1). Figure 5 shows the temperature variation of the intensity of the quasielastic scattering and the half-width at half-maximum (HWHM) of the least-squares fit. The Lorentzian width gives the time scale of fluctuating magnetic moments. We interpret the quasielastic scattering as being due to the fluctuating disordered Ho electronic magnetic moments. Only the large electronic magnetic moment of the Ho ions which is of the order of about 10 $\mu_B$ can give rise to such huge
amount of quasielastic scattering. At low temperature the intensity of the quasielastic scattering is small because of the magnetic ordering of the Ho ions. At higher temperatures the magnetic moments become gradually disordered and therefore the fluctuations increase. The decreasing intensity at higher temperature may only indicate that the quasielastic scattering goes out of the energy window of the instrument and is therefore only partially integrated. The half-width at half-maximum (HWHM) decreases at first with increasing temperature and then increases rapidly at higher temperatures. We expect the HWHM of the quasielastic scattering to increase at higher temperatures but the details of the temperature variation of the HWHM are not yet understood. Ehlers et al [17] have also observed huge quasielastic scattering in Ho$_2$Ti$_2$O$_7$ and have interpreted it as being due to the fluctuating electronic moments of the Ho ions but have neither fitted their quasielastic data nor given any quantitative explanations.

The present high resolution neutron spectroscopic investigation shows clearly the following new results on HoCrO$_3$: (1) the appearance of inelastic peaks at lower temperatures whose energies remain more or less constant in the temperature range 1.5–40 K, (2) the apparent sudden disappearance of these peaks at higher temperatures, and (3) the simultaneous appearance of increasingly strong quasielastic scattering. We attempt to rationalize these three main findings of our investigations. We wish to emphasize that most of the compounds for which hyperfine interaction has been investigated using high resolution inelastic neutron scattering contain only one type of magnetic ion. Here, for HoCrO$_3$, we have a much more complex situation. It contains two magnetic sublattices. The magnetic ordering HoCrO$_3$ is known to be very complex [25]. It is known that the Cr sublattice orders at $T_N \approx 142$ K. It is expected that Ho ions will get polarized in the field of the Cr sublattice also below $T_N \approx 142$ K. On cooling, both Cr and consequently Ho moments should increase. At low temperatures, both Cr and Ho moments should attain the saturation moment. It is still a bit surprising that the energy of the inelastic signal does not decrease significantly as a function of increasing temperature up to 40 K. The energy is expected to decrease with increasing temperature in the same way as the ordered Ho moment. This is not the case if we compare the present results with the intensity variation of the (100) magnetic reflection arising due to the Ho moment as determined by Shamir [25]. The intensity of the (100) magnetic reflection decreases at 40 K to about 30% of the low temperature intensity. We expect the magnetic moment of Ho to decrease to about 10% of the low temperature value. The energy of the inelastic peak is also therefore expected to decrease to about 10% of the saturation value. This is obviously not the case. One must however admit that due to the appearance of quasielastic scattering the quality of the fits becomes increasingly poorer at higher temperature. The sudden disappearance of the inelastic peak at higher temperature may be explained by noting that the inelastic peak gets hidden behind the quasielastic signal. Now we come to the possible origin of the strong quasielastic scattering at higher temperatures shown in figure 5. We already noted that Ehlers et al [17] have also observed similar huge quasielastic scattering in Ho$_2$Ti$_2$O$_7$ and they have interpreted it as being due to the fluctuating electronic moments of the Ho ions. The quasielastic scattering in HoCrO$_3$ can also have the same origin, as we discussed before. However it is known that HoCrO$_3$ has the first crystal-field excitation energy [33] at about 1.5 $\mu$eV. At higher temperature this crystal-field excitation may also lead to the quasielastic scattering observed by us.

In conclusion, we have observed low energy nuclear spin excitations in HoCrO$_3$ and have found quite different temperature dependences of the energy and intensity compared to those that we investigated previously. We have also observed huge quasielastic scattering which may arise due to the fluctuating electronic moments of the Ho ions that get increasingly disordered at higher temperatures or may be related to the first low energy crystal-field excitations.

Figure 5. Temperature variation of the energy and intensity and half-width at half-maximum (HWHM) of the quasielastic scattering of HoCrO$_3$. The least-squares error bars are smaller than the symbols or of about the same size. The continuous curves are just guides to the eye.
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