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Inelastic Neutron Scattering in Multiferroic Materials

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In order to obtain a deeper understanding of the spin interactions between the magnetic moments of the Tb-ions and the Mn-ions in multiferroic $TbMnO_3$, inelastic neutron scattering experiments (at the ILL in Grenoble and the Bragg Institute at ANSTO) are performed on isostructural, non-multiferroic $TbVO_3$. Acoustic and optical magnon branches are identified at energies comparable to the spin wave excitation spectrum of YVO_3. In addition, a crystal field excitation arising from the Tb-ions is identified at the energy of 14.9 meV. This is substantially larger than the crystal field excitation at 4.5 meV in $TbMnO_3$.

1. Introduction

Magnetism and ferroelectricity are both exciting physical properties and are used in everyday life in sensors and data storage [1]. Magnetic order occurs when the magnetic spin of the atoms are aligned in a periodic manner. Electric polarization is caused by a uniform displacement of an electronic configuration in a well defined direction. Multiferroic materials are materials where both properties coexist. They offer great potential for future technological applications such as increased data storage capacity or novel sensors. In principal, data storage capacity can be increased via the coexistence of electric and magnetic polarizations, thus replacing the current 2-bit system with a 4-bit memory system [2]. In some multiferroic materials, such as $TbMnO_3$, the two order parameters (electric polarization and magnetic order) are coupled. This allows for a direct switching of both properties. At present, the underlying mechanism for this coupling is not fully understood.

$TbMnO_3$ belongs to the class of orthorhombically distorted perovskites with the space group *Pbnm*. This structure consists of a network of corner-sharing MnO_6 octahedra with Tb-ions spaced between them. The octahedra are typically tilted and distorted, caused by the Jahn-Teller effect. The room temperature lattice parameters are a = 5.30 Å, b = 5.86 Å and c = 7.49 Å [3]. $TbMnO_3$ undergoes three magnetic phase transitions. Below 43 K the spins of the Mn-ions exhibit an incommensurate sinusoidal magnetic structure. Upon further cooling the spin structure changes at T = 25 K to a cycloidal spin structure where the spins rotate around the *a*-axis, i.e. within the *bc*-plane [4]. This phase transition is accompanied with the onset of the ferroelectric order. Finally, below 8 K the moments of the Tb-ions order ferromagnetically along the *b*-axis with an additional antiferromagnetic coupling between nearest-neighbor Tb-spins along the [110] direction [4]. In order to obtain a deeper understanding of the spin interactions between the Tb-moments and the Mn-moments, we have performed neutron

scattering experiments on the non-multiferroic material $TbVO_3$. Both materials, $TbMnO_3$ and $TbVO_3$, crystallize in the same three-dimensional perovskite crystal structure *Pbnm*, but possess a different electronic configuration, i.e. there are two electrons in the 3d electronic level of $TbVO_3$ in contrast to four in $TbMnO_3$. The spin structure of $TbVO_3$ is C-type antiferromagnetic below 110 K [5-8], whereas the Tb-moments exhibit a non-collinear order below 11 K [8]. However, $TbVO_3$ does not exhibit an electric polarization down to the lowest temperatures.

2. Experimental details

Large high quality single crystals of $TbVO_3$ were grown by the travelling solvent floating-zone technique using an infrared mirror furnace. Details of the growth process are described by Miyasaka and Fujioka [5-7]. The inelastic neutron scattering experiments were performed on the triple-axis spectrometers IN8 and IN22 at the Institut Laue Langevin in Grenoble, France and at the instrument TAIPAN at the research reactor OPAL at ANSTO. A pyrolithic graphite PG 002 monochromator and analyzer were used with a setting of the final wavelength of k_f = 2.662 $Å^{-1}$. In order to suppress second order scattering, a PG-filter was placed before the analyzer.

3. Results

A contour plot of the inelastic neutron scattering data is presented in Fig. 1. The data were taken along the $(0,0,Q_L)$ direction starting from the zone centre (½, ½, 1) of the C-type antiferromagnetic Brillouin zone. Note that, as in ref. [9], the pseudo-cubic notation with $a^*=a/\sqrt{2}$, $b^*=b/\sqrt{2}$, and $c^*=c/2$ is used. The data were taken at 40 K, a temperature where the V-moments are ordered, but still above the magnetic ordering temperature of the Tb-sub-lattice. Three distinct branches are observed: a dispersive excitation between 5.0 meV and 12 meV, an intense and dispersionless excitation at 14.9 meV, and a weakly dispersive branch

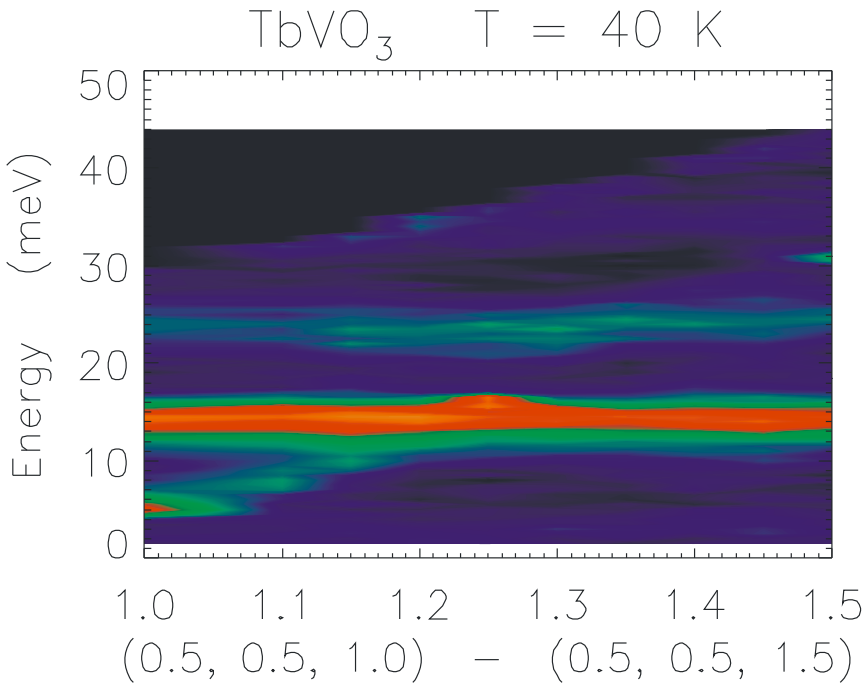

Fig. 1: Contour plot of the inelastic neutron scattering data of $TbVO_3$ along the $(0,0,Q_L)$ direction of the C-type antiferromagnetic Brillouin zone. The data were taken at a temperature of 40 K, i.e. within the C-type magnetic phase of $TbVO_3$, but well above the ordering temperature of the Tb-moments.

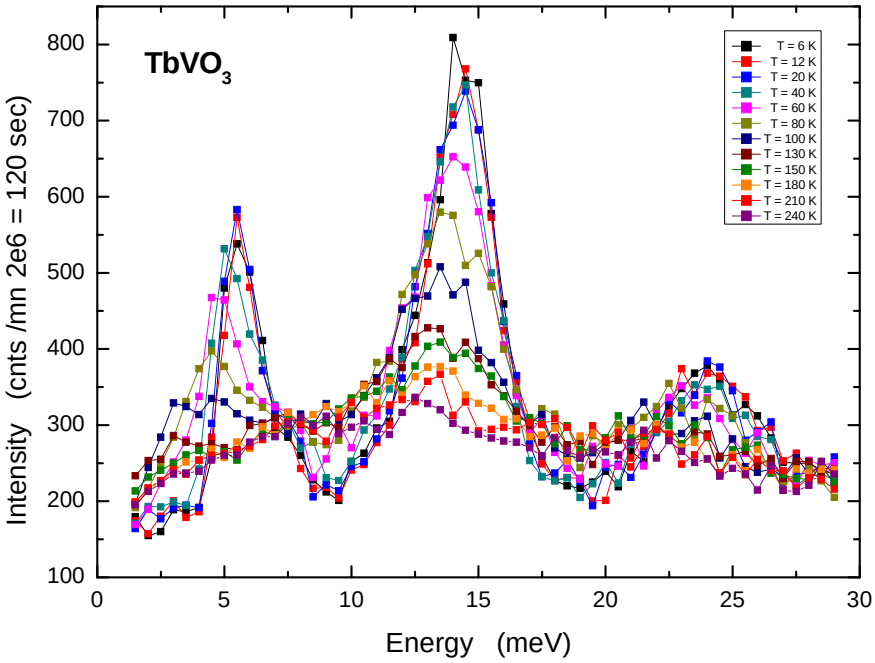

Fig. 2: Temperature dependence of the inelastic neutron scattering spectrum spectrum of $TbVO_3$ at the centre of the magnetic Brillouin zone, i.e. at (½ ½ 1).

between 24.3 meV and 25.6 meV. In order to identify the different excitations, we have investigated the temperature dependence of the inelastic neutron scattering spectrum at the centre of the magnetic Brillouin zone at (½, ½, 1).

Fig. 2 shows the temperature dependence of the spectrum at the centre of the C-type antiferromagnetic Brillouin zone. The peaks at 5.5 meV can be attributed to a spin wave excitation. This mode completely disappears at the magnetic phase transition temperature of 110 K. Furthermore, the energy bandwidth of this mode is in accordance with that of the acoustic magnon branch observed in YVO_3 (see ref. [9]). The mode at 14.9 meV exhibits a different behaviour. This excitation is dispersionless in energy, linewidth, and intensity. Furthermore, the mode does not completely disappear above the magnetic phase transition. Therefore, this mode cannot be associated with a magnetic excitation. A comparison with the Raman light scattering data obtained on $NdVO_3$ and $LaVO_3$ indicates that the lowest energy optical phonon modes should appear at an energy above 20 meV [10]. Thus, this mode cannot be associated with a lattice vibration. Therefore, the excitation at 14.9 meV can be attributed to a crystal field excitation arising from the Tb-moments. From its temperature dependence the weakly dispersive mode between 24.3 meV and 25.6 meV can be attributed to spin excitations. This energy is also in close to that of the optical magnon branch observed in YVO_3 which appears between 16 meV and 20 meV. A weak inelastic signal remains above the magnetic phase transition temperature at an energy of 22 meV. This weak contribution can be associated with the lowest energy optical phonon branch of $TbVO_3$ and originates from the vibration of the Tb-atoms.

The resulting dispersion relation of the excitation spectrum of $TbVO_3$ is shown on the left side of Fig. 3. For comparison, the spin wave dispersion and crystal field excitation spectrum of $TbMnO_3$, measured by Senff *et al.* [11], is shown on the right. The overall magnon bandwidth of the acoustic magnon branch in $TbVO_3$ is comparable to the spin excitations in $TbMnO_3$. As in YVO_3, a splitting into an acoustic and an optical magnon branch is observed. The presence of a magnon splitting served as the main argument for the existence of an 'orbital Peierls state' in YVO_3 [9,12,13].

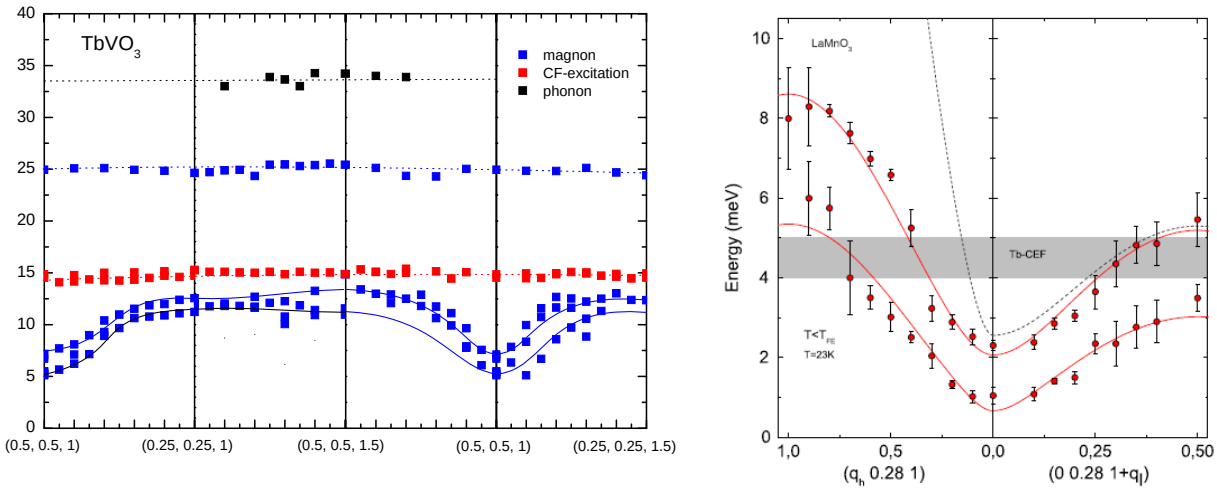

Fig. 3. Spin wave dispersion relation of $TbVO_3$ taken at 40 K (left). The blue symbols can be associated with spin wave excitations, whereas the black symbols correspond to phonons. The red symbols denote excitations arising from a crystal field excitation of the Tb-ions. For comparison, the spin wave dispersion and crystal field excitation spectrum of $TbMnO_3$, measured by D. Senff *et al*. [11], is shown on the right.

4. Conclusions

In conclusion, we have determined the dispersion relation of the excitation spectrum of $TbVO_3$. An acoustic and an optical magnon branch are identified at comparable energies as in the spin wave excitation spectrum of YVO_3. Furthermore, a crystal field excitation arising from the Tb-ions is identified at an energy of 14.9 meV. This is substantially larger than the crystal field excitation at 4.5 meV in isostructural $TbMnO_3$. These data can serve as an important input for future calculations of the crystal field excitation spectrum in both $TbMnO_3$ and $TbVO_3$ and can thus provide significant information about the electronic and magnetic structures of both materials.

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