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Spin lattice coupling in multiferroic hexagonal $YMnO_3$

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Abstract. Aiming to shed light on the possible existence of hybrid phonon–magnon excitations in multiferroic manganites, neutron scattering measurements have been undertaken at LLB and ILL on the particular case of hexagonal $YMnO_3$. Our experiments focused on a transverse acoustic phonon mode polarized along the ferroelectric axis. The neutron data show that below the magnetic transition, this particular phonon mode splits in two different branches. The upper branch is found to coincide with a spin wave mode. This manifestation of a strong spin-lattice coupling is discussed in terms of a possible hybridization between the two types of elementary excitations, the phonon and magnons.

Keywords. Multiferroic; manganites; spin phonon hybridization; inelastic neutron scattering.

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1. Introduction

The $RMnO_3$ manganites (R is a rare earth) form a rich class of materials, exhibiting a large variety of physical properties, ranging from charge segregation and colossal magnetoresistance in the case of $LaMnO_3$ to the so-called multiferroic behaviour in the case of smaller radius rare earth. These last materials have drawn a lot of attention recently in the solid-state physics community, as their ground state is characterized by coupled ferroelectric and magnetic orderings [1–3]. Indeed, since coupling these two order parameters allows the reversal of the ferroelectric polarization by applying a magnetic field or the control of the magnetic order parameter by an electric field, these materials may lead to very promising technological applications, offering the possibility to design novel spintronic devices [4]. Moreover, the very nature of the interplay between magnetic ordering and ferroelectricity in these compounds is at the moment one of the puzzling fundamental questions in condensed matter physics.

Aiming to get insight into this fascinating problem, neutron scattering techniques (diffraction and inelastic scattering) are particularly powerful, since they offer the possibility to determine with a high accuracy the atomic displacements, the magnetic structure, and the associated dynamics. Because of the coupling between lattice distortions and magnetism, a strong interaction between elementary excitations (phonons and spin waves) is expected in these materials. In this paper, we focus on the particular case of $YMnO_3$ and report neutron data showing evidence for this interplay. The data show the opening of a gap, at low temperature in the dispersion of a transverse acoustic phonon mode polarized along the ferroelectric c-axis and propagating along a^*. This gap opens below the Néel temperature T_N due to some coupling with the magnetic subsystem [5].

The $RMnO_3$ manganites can be divided in two subclasses, depending on the R-element. Indeed, as one moves along the 4f serie, the decrease of the R-element size induces a crystallographic change from an orthorhombic (R = Pr, Nd, Sm, Eu, Gd and Tb) to a hexagonal (R = Ho, Er, Tm, Yb, Lu, Y, Sc and In) structure. The multiferroic transition in the orthorhombic case is currently understood with the help of two key ingredients [6,7]. First, magnetic frustratio +n due to competing exchange integrals between successive neighbours stabilizes a spiral magnetic phase below the Néel temperature T_N. Next, to lower the Dzyaloshinskii–Moriya interaction, oxygen atoms are pushed off the Mn–Mn bond, driving an electric polarization at T_N. As a result, this particular spin-lattice coupling mixes a polar phonon and spin waves involving deviations out of the spiral magnetic plane. This mode is thought to be the Goldstone mode of the multiferroic transition. The possible existence of such a hybridized excitation has been reported very recently in orthorhombic $GdMnO_3$ and $TbMnO_3$ [8]. These authors have interpreted their infra-red spectroscopy measurements in terms of 'electromagnons', hybridized magnetic and phononic low energy excitations (at 2.48 meV). This result, together with the analysis given in [6], agrees with the neutron study by Senff *et al* [9], which identifies the electromagnon with a spin wave mode observed at the same energy.

The hexagonal $RMnO_3$ are likely to come under different physics. Indeed, the ferroelectric and magnetic orderings are no more concomitant since the electric polarization appears far above room temperature ($T_c \sim 900$ K and $T_N \sim 100$ K). Nevertheless, evidence for a strong interplay between magnetic and ferroelectric order parameters has been shown by dielectric constant measurements, showing anomalies arising at T_N [10–12], diffraction techniques showing evidence for an enhancement of the electric moment below T_N [13]. More recently, various experiments as thermal expansion [14], thermal conductivity measurements [15], or Raman scattering [16], have pointed out the existence of a 'giant' spin-lattice coupling, that could be responsible for this interplay. Its microscopic origin remains however an open question.

Hexagonal $RMnO_3$ are formed by stacked Mn–O and R–O layers. The Mn ions are surrounded by three in-plane and two apical oxygen ions (MnO_5 bipyramid) and form a triangular lattice (figure 1). The in-plane oxygen ions sit at two different crystallographic sites, called O3 and O4. The ferroelectric distortion can be roughly understood as the combination of spontaneous tilting of the MnO_5 bipyramids along the O3O4 direction accompanied by a buckling of the Y–O planes. As a result, oxygen and yttrium atoms move off the hexagonal planes along the c-axis in

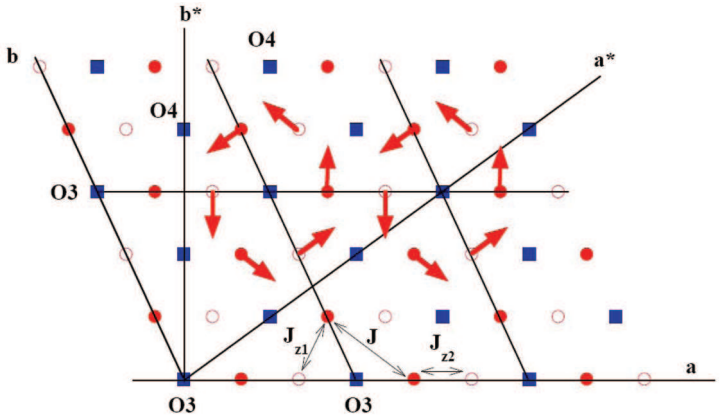

Figure 1. Schematic view of spin ordering [19] and atomic positions in $YMnO_3$. The squares depict oxygen O3 and O4 positions, while the circles indicate Mn position (filled and open symbols correspond respectively to the $z = 0$ and the $z = 1/2$ plane). The magnetic and chemical unit cells are identical with lattice parameters $a = 6.14$ Å and $c = 11.39$ Å.

opposite directions, giving rise to staggered ferroelectric moments. Since there are two O4 ions and only one O3 per Mn–O plane, the chemical unit cell finally acquires a net moment [17]. The Mn spins order antiferromagnetically below $T_N = 72$ K, the spins lying in the hexagonal plane (see figure 1). Note that there has been a long debate concerning the direction of the spins, parallel or orthogonal to the Mn–O. Indeed both structures are homomorphic, and very difficult to distinguish [18–20].

High quality $YMnO_3$ single crystals of about 0.4 cm^3 have been grown using the standard floating zone technique. The neutron scattering experiments have been carried out on cold and thermal triple-axis spectrometers at the Orphée-LLB reactor and at the Institut Laue Langevin. In all experiments, the crystal was placed in a closed-cycled refrigerator or in a cryostat, and oriented with (1 0 0) and (0 0 1) wave vectors in the horizontal scattering plane. Bent or flat PG and Cu crystals were used as monochromator and analyzer, depending on the desired resolution. Open collimations were used to fully benefit from the focusing effects.

The spin dynamics have been studied by taking constant-Q scans at different temperatures, leading to the spin wave dispersions reported in figure 2. Data were also collected to study the dispersion and the exchange coupling along the c-axis. These measurements mainly confirm the results reported in refs [21–23]. However, detailed comparison of the neutron intensities with calculations of the magnetic dynamical structure factor enabled us to improve the understanding of the spin excitations in this frustrated system. Indeed, the in-plane or out-of-plane nature of the spin fluctuations induces modulations of the neutron intensities as a function of Q. This information was used to choose the best experimental conditions able to reveal properly each different spin wave mode. This enabled to distinguish the high energy spin wave modes 1 and 2 unresolved in [22]. The data are described by the following spin Hamiltonian based on the Heisenberg model $H = JS_iS_j - hS_in_i + DS_i^zS_j^z$. J describes the scalar exchange interaction, while h and D correspond to

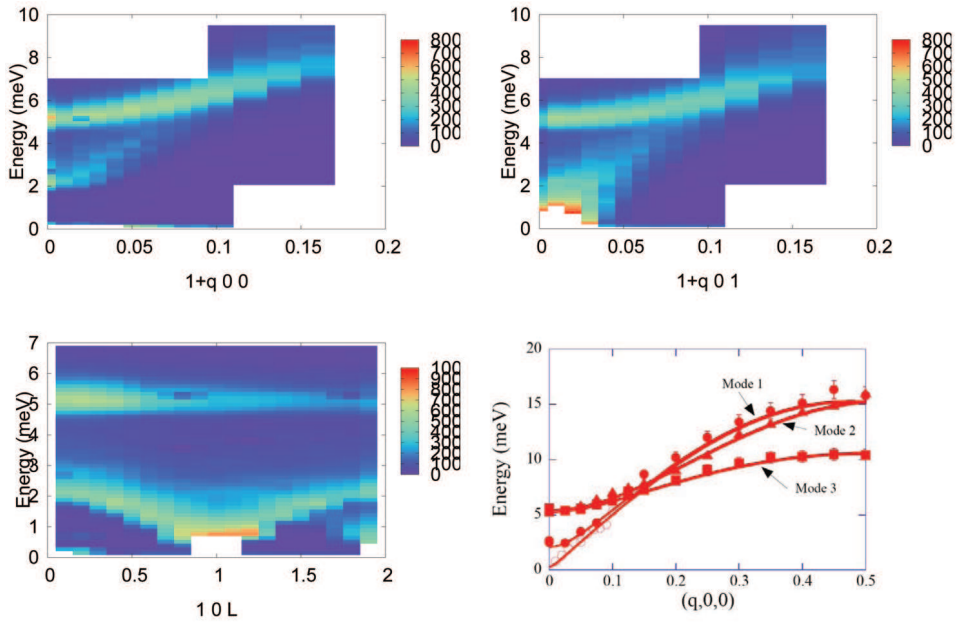

Figure 2. Upper panel: Colour mapping of the neutron intensity measured as a function of energy and wave vector along a^*. Left and right pictures correspond to data taken around (1 0 0) and (1 0 1) Bragg positions respectively. Lower left panel: Colour mapping of the neutron intensity measured as a function of energy and wave vector along c^*. Lower right panel: Magnon dispersions along a^*. Solid lines are fits to the data according to the Heisenberg model (see text). Mode 1 (closed circles) has been measured around (1 0 0) where it corresponds to out-of-plane fluctuations. The open circles correspond to the same branch measured around the (1 0 1) Brillouin zone. The decrease of the zone centre gap is due to exchange along the c direction. Modes 2 and 3 (triangles and squares) have been measured around (0 0 6) where they correspond to in-plane fluctuations.

easy-axis and easy-plane anisotropies respectively. S_i denotes the spin at magnetic site while n_i is a unit vector pointing towards the direction of the ordered spin at the same site. A good global agreement is obtained if the antiferromagnetic interaction between in-plane nearest neighbours is set to $J = 2.3$ meV. Two gaps are observed at the zones centres: the large one ($\sim$5 meV) is well reproduced with an easy plane anisotropy $D = 0.33$ meV. Interestingly, we observe a decrease of the second one, from 2.5 meV around the (1 0 0) Bragg peak down to 0.28 meV around (1 0 1). This very small value was obtained with a good accuracy by taking data with a small final neutron energy ($kf = 1.2$), ensuring a very high resolution. From this value, we get a vanishingly small easy axis anisotropy $h = 0.0008$ meV. The 2.5 meV gap is described by introducing two exchange couplings Jz_1 and Jz_2 (see figure 1) between Mn spins belonging to adjacent layers. From the value of the gap, we obtain $Jz_1 - Jz_2$ in the range 0.01 to 0.015 meV. Jz_1 is thus ferromagnetic and larger than Jz_2, in agreement with the magnetic structure. To get Jz_1 and

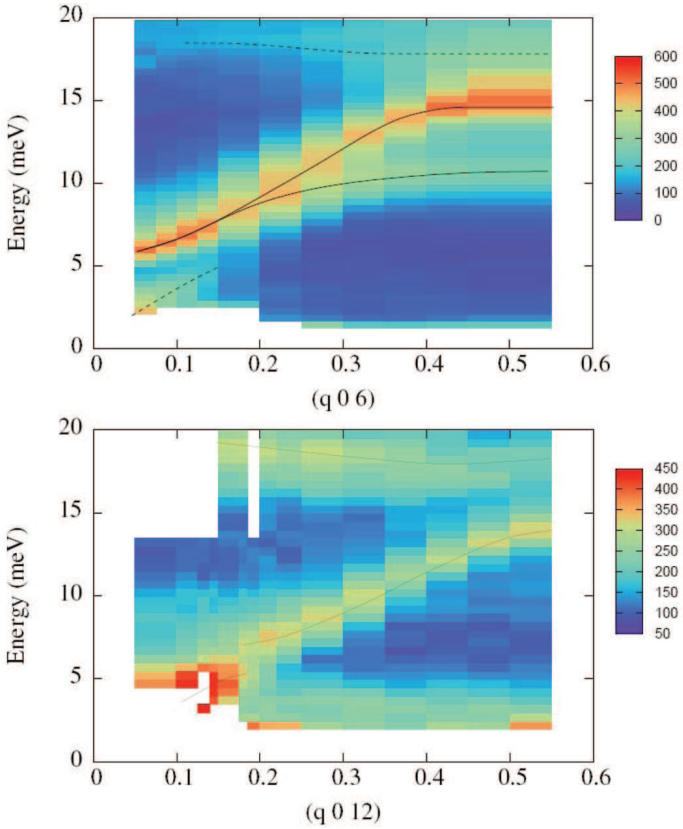

Figure 3. Colour mappings of the neutron intensity obtained as a function of energy transfer and wave vector along a^*. The data were taken at $T = 18$ K around $(0, 0, 6)$ Bragg position (upper panel) and around $(0, 0, 12)$ (lower panel). Solid and dashed lines are guides to the eyes.

Jz_2 separately turns out to be very difficult. Since these couplings are expected to lift the degeneracy of the 5 meV mode (large gap), the 5 meV peak was fitted with two instead of one modes. This procedure gives the following rough estimates $Jz_1 \sim 0.025$ meV and $Jz_2 \sim 0.01$–0.015 meV.

We now turn to the description of the interplay between the spin and lattice dynamics. We focus on a particular transverse phonon mode (mainly) polarized along the ferroelectric c-axis and propagating along a^* (see figure 1). It is worth noting that a^* coincide with the O3–O4 buckling direction associated with the ferroelectric distortion. This phonon is thus expected to be closely related to ferroelectricity. Its dispersion was studied thanks to constant-Q scans performed at $(q, 0, 6)$ and $(q, 0, 12)$ with thermal as well as cold neutrons. These scans allow the determination of this transverse acoustic mode, as well as the dispersion of a roughly flat optic mode. The optic mode energy is about 18 meV, which is in good agreement with the Raman experiments reported in [24]. Below T_N, the different spin wave branches give rise to strong magnetic scattering discussed above. As shown on the

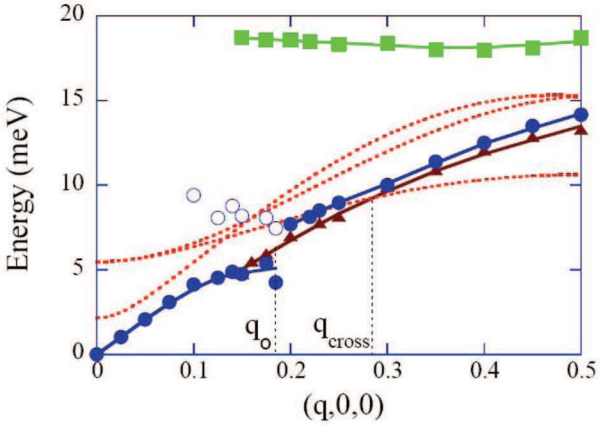

Figure 4. Phonon dispersions obtained at 200 K (triangles) and 18 K (circles). Closed and open symbols correspond to large and small intensities respectively. The squares correspond to the optic phonon mode. Red dotted lines are calculated spin wave dispersions. The gap in the phonon dispersion opens at q_0. Crossing of the 200 K phonon dispersion with the spin wave mode 3 arises at $q_{\rm cross} \sim 0.3$.

upper panel of figure 3, this signal is strong enough to hide the acoustic phonon mode beyond $q = 0.15$, except at small q (see the dotted line). Taking advantage of the decrease of the magnetic form factor as a function of $|Q|$, the measurements around $(q, 0, 12)$ (lower panel) allow to fully eliminate the magnetic scattering and thus to reveal the complete dispersion of the acoustic phonon mode. A close examination of the region around $q_0 \sim 0.185$, $\omega = 6$ meV shows that the acoustic phonon dispersion exhibits at low temperature a gap around q_0. It is accompanied by the expected intensity balance between the lower and the upper branches. Bringing together different measurements as well as the fitted spin waves, we obtain the low temperature dispersions shown in figure 4. Further examination of the data shows that the spin wave mode 3 and the upper acoustic phonon branch essentially coincide around q_0. The closure of the gap was studied by following the same experimental procedure at different temperatures up to 200 K. From this temperature dependence, we conclude that the gap opens mainly below $T_{\rm N}$, showing its connection with the magnetic subsystem.

If collecting data at large Q vectors is a sort of trick that works pretty well, it is clear that the best way to demonstrate the existence of the gap is to repeat these measurements with spin polarization analysis. This work was done recently on IN22 at the Institut Laue Langevin. The obtained results are in perfect agreement with the present data, confirming the existence of the phonon gap [25].

Let us now turn to the interpretation of these data. Some clues can be found by considering, for example, similarities of the present experiments with ferrous halides [26]. Indeed, in these materials, a valuable picture of both anomalous behaviour of the thermal conductivity [27] and neutron scattering data [28,29] has been proposed on the basis of single-ion magnetostriction, arising from modulation of the crystalline field by the motion of nonmagnetic ions [30]. This interaction

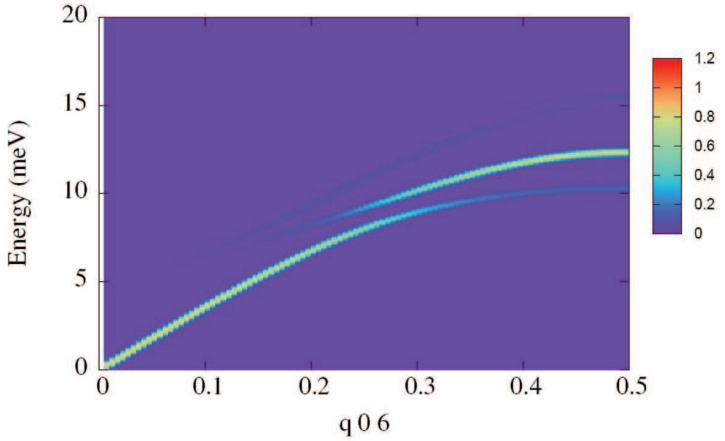

Figure 5. Nuclear dynamical structure factor (in arbitrary units) calculated as a function of energy and wave vector along $(q, 0, 6)$. See text for the description of the model.

couples the spins and the atomic displacements via the local deformation, being in turn linear in the creation and annihilation of phonon operators. In addition, it involves products of two off-diagonal spin components, giving rise to linear terms in the spin wave operators as well. In the magnetically ordered phase, these linear terms are known to give rise to a resonant interaction and in turn to the hybridization of the phonon and the spin waves [27,31]. In the case of $YMnO_3$, considering only the coupling with the studied transverse phonon branch, the model basically predicts the hybridization between the phonon and the spin wave mode 3. This results in the emergence of magneto-elastic modes, separated by a gap opening at the crossing point between the bare dispersions, namely at $q_{\text{cross}} \sim 0.3$. Figure 5 shows a calculation of the nuclear dynamical structure factor revealing the phonon-like component of the hybrid excitations. In principle, it can be directly compared with the neutron data shown in the lower panel of figure 3. The calculation shows a jump from the lower to the upper mode, providing a natural interpretation for the experimentally observed gap. The main difference which is not understood so far, comes from the value of the wave vector q_0 which is slightly smaller that the theoretical q_{cross}.

These results should be discussed also in the framework of the model developed for orthorhombic systems. In these systems, the Dzyaloshinskii–Moriya interaction plays a fundamental role, pushing the oxygen atoms off the Mn–Mn bond and giving rise to the ferroelectric distortion. The hybridization is expected between a polar (optic) phonon and the spin wave mode involving spin fluctuation pointing out of the spiral plane. In the present hexagonal case, the Dzyaloshinskii–Moriya is relevant also, simply by symmetry considerations. Similar oxygen displacements are thus possible. However, due to the triangular symmetry (each oxygen ion is located at the centre of the triangle formed by three neighbouring Mn ions) and due to the planar arrangement of the spins, the net force experienced by this oxygen atom is zero. As a result, the orthorhombic mechanism does not hold in the hexagonal case as far as static displacements are concerned. What about the dynamics? It

must be emphasized that the cross product $Si \times Sj$ typical of this interaction involves products of two off-diagonal spin components, while its D vector involves atomic displacements. As a result, this interaction is linear in phonon and spin wave operators, leading potentially to the desired hybridization. Specific theoretical work is necessary to clarify this issue, but it is clear that one could find here an overall picture able to describe orthorhombic and hexagonal systems.

In summary, besides the detailed study of the spin wave branches in $YMnO_3$, our neutron experiments provide evidence for the opening of a gap below T_N in the dispersion of the transverse acoustic phonon mode polarized along the ferroelectric axis. The upper phonon branch is found to lock on one of the spin wave modes. These data reveal that a strong coupling between spins and phonons is at play in this hexagonal multiferroic material. These findings are discussed in terms of a possible hybridization between the two types of elementary excitations.

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