

Magneto-Elastic Interactions in Complex Materials

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ABSTRACT

In order to investigate magneto-elastic coupling through the series of magnetic ordering-induced transitions in a geometrically-frustrated multiferroic material, we measured the vibrational properties of DyMn₂O₅ as a function of temperature and applied magnetic field. This work reveals the dynamic nature of the local structural response, changes that we analyze in terms of calculated mode displacements and local lattice distortions.

INTRODUCTION

The interplay between magnetism and structure is of great current interest as it may hold the key to understanding functionality in complex materials. We are now starting to understand that even “simple” magnetic ordering transitions such as the antiferromagnetic to ferromagnetic transition may take place with important magneto-elastic interactions. More complex magnetic ordering transitions involving the development of non-collinear magnetic states are also starting to yield their secrets. In both simple and complex situations, x-ray, heat capacity, dielectric constant, and thermal conductivity measurements elucidate important magneto-elastic coupling effects at various magnetic ordering transitions, but as bulk techniques, they probe only an average lattice response. Extending this work to include an understanding of the microscopic response of the lattice (i.e. local changes in bond lengths and angles) is important for unraveling the local distortions that take place due to coupling with a particular magnetic state. The challenge is that local lattice distortions are predicted to be very small, making high-sensitivity measurements a necessity.^{1,2} As a consequence, strongly coupled materials such as the multiferroics present the best opportunity to observe and elucidate these effects.

In this talk, I will illustrate the use of vibrational spectroscopy to probe local lattice distortions in two different systems. The first example will focus on a simple ferromagnetic transition coupled to magneto-elastic interactions. The second example will involve magneto-

elastic interactions in DyMn_2O_5 , a geometrically-frustrated multiferroic material. The latter case is summarized here.^{3,4}

METHODS

Small pieces of single crystals were mixed with paraffin to form isotropic pellets. The infrared response of DyMn_2O_5 was measured as a function of temperature and magnetic field as described previously.^{3,4} Both absolute absorption $\alpha(\omega)$ and absorption difference spectra $[(\alpha(\omega, H) - \alpha(\omega, H = 0))/\alpha(\omega, H = 0)]$ are employed to illustrate changes through various magnetic ordering transitions. The absorption difference curves are especially useful for elucidating small spectral changes. We also carried out complementary lattice dynamical calculations and used the predicted mode displacement patterns to understand the local structure modifications.

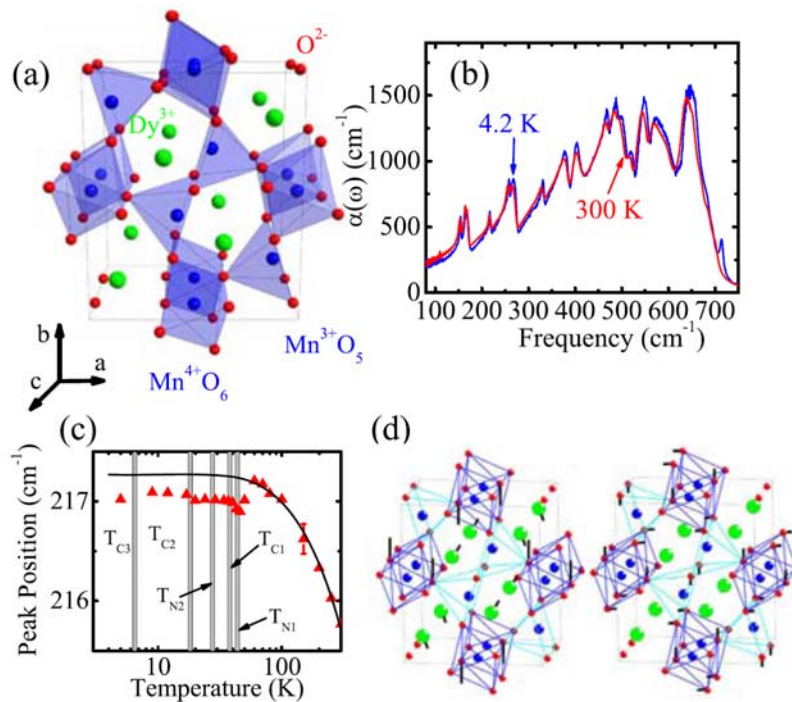


Figure 1: (a) 300 K crystal structure of geometrically-frustrated DyMn_2O_5 showing distorted Mn^{4+}O_6 ($S = 3/2$) octahedra cross linked with distorted Mn^{3+}O_5 ($S = 2$) square pyramids. (b) Absolute absorption spectrum at two different temperatures. (c) Peak position vs. temperature of a representative feature in the vibrational spectrum. The solid line is a fit to the high-temperature anharmonic response, and the gray vertical lines denote magnetic ordering temperatures. (d) Representative mode displacement patterns obtained from our molecular dynamics calculations for features calculated to be at 208 and 231 cm^{-1} .

RESULTS AND DISCUSSION

DyMn_2O_5 displays an orthorhombic crystal structure.⁵ It is comprised of slightly distorted, linked Mn^{4+}O_6 and Mn^{3+}O_5 building block units as shown in Fig. 1(a). Because the Mn^{3+} ($S = 2$) and Mn^{4+} ($S = 3/2$) spins are geometrically frustrated, it displays a rich magnetic field-temperature ($H - T$) phase diagram.⁶⁻⁹ With decreasing temperature, the series of magnetic

ordering-induced phases includes: antiferromagnetic order with an incommensurate magnetic modulation below 43 K, a lock-in transition into a commensurate ferroelectric phase at 39 K, spin reorientation transitions at 27 and 18 K, and a reentrant commensurate magnetic state at 6.5 K that involves ordering of the Dy^{3+} moments.⁶⁻⁹ It is interesting to note that several of the infrared active vibrational modes in DyMn_2O_5 are sensitive to this cascade of transitions, as illustrated in Fig. 1(c) for the 217 cm^{-1} mode.⁴ These small frequency shifts demonstrate that the lattice is not rigid through the series of magnetic ordering transitions. Further, they can be used to extract spin-lattice coupling constants as discussed elsewhere.⁴

Application of a magnetic field also offers an opportunity to tune competing interactions in a material and drive through different magnetic transitions. In DyMn_2O_5 , these include: paraelectric to ferroelectric-3 ($H \parallel a$ or b) at 1.5 T, paraelectric to high field ($H \parallel c$) at 4 T, and ferroelectric-3 to ferroelectric-2 ($H \parallel b$) at 8.5 T.⁶⁻⁹ A discussion of characteristic high frequency modes, most notably those that display well-defined local distortions and as a consequence modify Mn-O-Mn superexchange interactions, is available in Refs. 3 and 4. Here, we illustrate that vibrational spectroscopy can provide specific information on the most important local lattice displacements and how they differ in various magnetic states by examining the behavior of the lowest frequency spectral features.

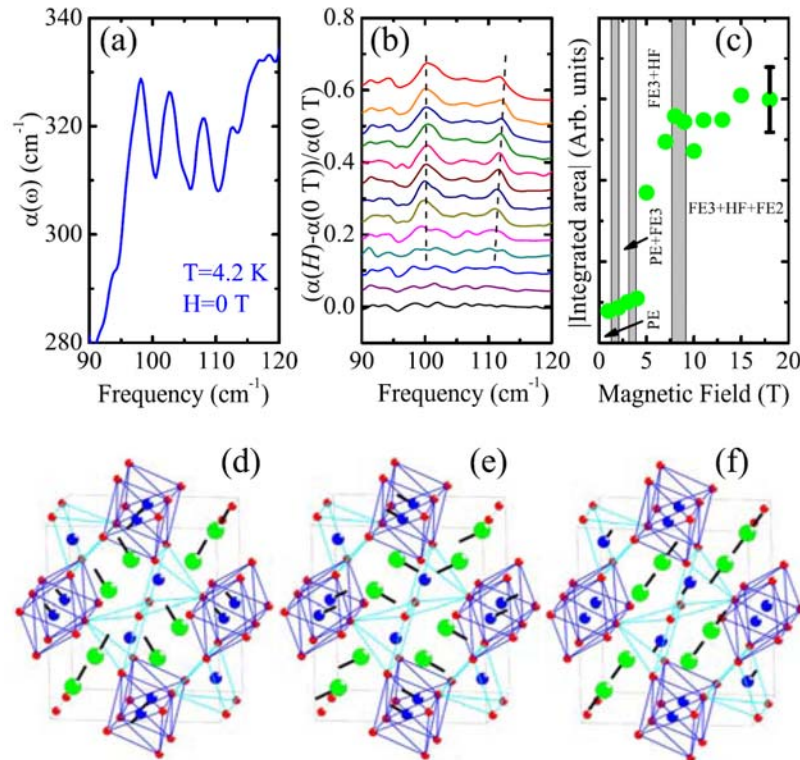


Figure 2: (a) Close-up view of the absolute absorption spectrum of DyMn_2O_5 at low temperature. (b) 4.2 K absorption difference spectra at $H = 1, 2, 3, 4, 5, 7, 8, 9, 10, 11, 13, 15,$ and 18 T , with curves offset for clarity. (c) Integrated area of the absorption difference spectra between ~ 95 and 115 cm^{-1} in (b) as a function of applied magnetic field. The vertical grey lines denote various field-induced phase boundaries, although the response is averaged for an isotropic sample. (d), (e) and (f) Displacement patterns for the low frequency modes of DyMn_2O_5 calculated to be at $95, 104,$ and 117 cm^{-1} , respectively. They involve large relative Dy^{3+} /polyhedral displacements.

As discussed above, an applied magnetic field drives DyMn_2O_5 through a series of different magnetic ground states. Analysis of absorption difference spectra of the lattice modes between 95 and 115 cm^{-1} and the associated changes in integrated area (Fig. 2) shows that Dy^{3+} /manganese oxide polyhedral displacement modes are sensitive to the $H \parallel c$ paraelectric to high field transition near 4 T. Analysis of absorption difference data, peak positions, and integrated areas of spectral features between 140 and 180 cm^{-1} (Fig. 3) shows that the ferroelectric-3 to ferroelectric-2 transition ($H \parallel b$) near 8.5 T is also associated with changes in the lattice. These observations provide clear evidence for strong spin-lattice coupling in this system and the role of relative MnO_6 and MnO_5 polyhedra motion with respect to Dy^{3+} centers.

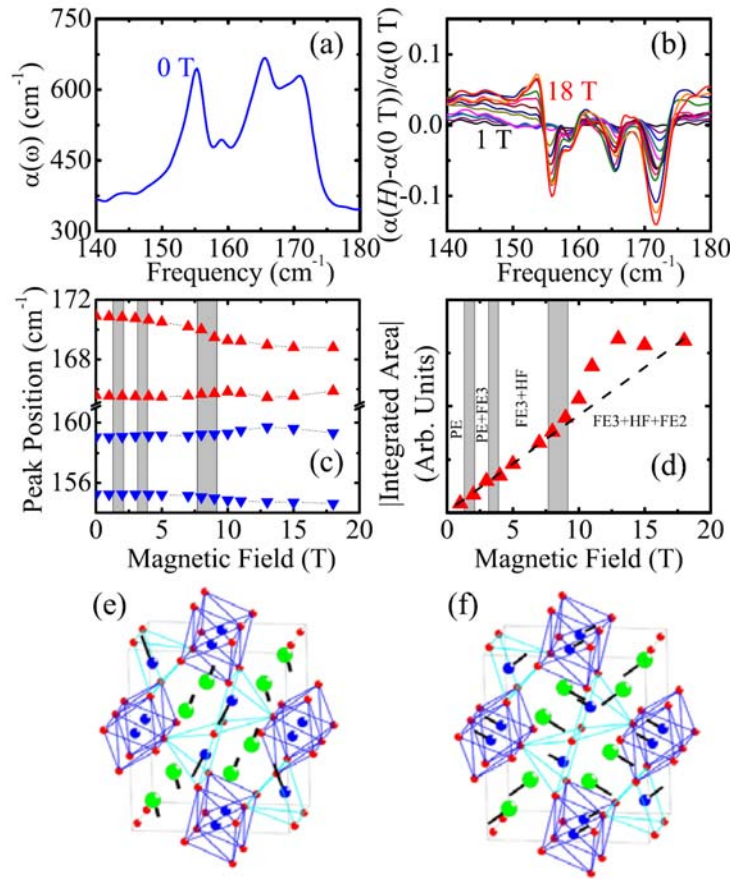


Figure 3: (a) Close-up view of the 4.2 K absorption spectrum of DyMn_2O_5 at zero magnetic field. (b) Absorption difference spectra at low temperature. (c) Magnetic field dependence of the peak positions. (d) Absolute value of the integrated area of the absorption difference spectra in the $140 - 180\text{ cm}^{-1}$ range. The gray vertical lines in (c) and (d) denote the critical fields, although the response is averaged for an isotropic sample. The dashed line in (d) is a guide to the eye. (e) and (f) Representative displacement patterns of calculated 170 and 176 cm^{-1} modes, respectively.

What are the consequences of this interplay between structure and magnetism for functionality? The static magneto-dielectric effect¹⁰ is certainly a prominent and potentially useful bulk property that gains strength from nearby dipole-allowed excitations. In DyMn_2O_5 , the static dielectric contrast, $\Delta\epsilon/\epsilon$, begins to grow above 4 T, displays $>100\%$ contrast at 7 T, and decreases at higher fields.¹⁰ Electromagnon¹¹ and crystal field excitations¹² have been shown to

contribute to this dispersive contrast. The low frequency field-dependent phonons identified here provide additional candidates of appropriate energy and symmetry, although the relative importance of each contribution to $\Delta\epsilon/\epsilon$ depends on both oscillator strength and proximity to the probe frequency (which is near the static limit in Ref. 10). The trio of low-frequency lattice modes between 95 and 115 cm^{-1} corresponding to relative Dy^{3+} /manganese oxide polyhedral displacements is sensitive to the paraelectric to high field ($H \parallel c$) transition at 4 T, where the static magneto-dielectric effect really begins to grow. This indicates that the new low symmetry state is more polarizable. $\Delta\epsilon/\epsilon$ reaches a maximum between 7 and 8 T, decreasing again after the ferroelectric-3 to ferroelectric-2 transition ($H \parallel b$) near 8.5 T.¹⁰ Spectral features between 140 and 180 cm^{-1} are associated with the 8.5 T transition indicating that changes in the lattice correlate with a less polarizable lattice and reduced dielectric contrast at high magnetic field.

CONCLUSIONS

Multiferroic DyMn_2O_5 is an excellent material for investigating magnetoelastic interactions and geometric frustration. Here, we demonstrate that low frequency lattice modes involving relative displacements of manganese oxide polyhedra, relative displacement of Dy^{3+} centers with respect to the polyhedra, and strong Mn motion are sensitive to magnetic ordering transitions driven by both temperature and magnetic field. We discuss correlations between the static magneto-dielectric contrast and the magneto-infrared response and how the field-driven lattice distortions may impact $\Delta\epsilon/\epsilon$.

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