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Phonon mode softening at the ferroelectric transition in $Eu_{0.5}Ba_{0.5}TiO_3$

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Abstract We have observed the effects of phonon mode softening at the ferroelectric transition in $Eu_{0.5}Ba_{0.5}TiO_3$ by ^{151}Eu Mössbauer spectroscopy. Both Eu^{2+} and Eu^{3+} spectral components are observed in the relative area ratio of 90% : 10% and both show a decrease in subspectral area at the transition, centred at 175 K, due to phonon mode softening. Surprisingly, the temperature dependence of the f-factor shows a much stronger response in the Eu^{3+} component than in the Eu^{2+} one. Preliminary analysis of neutron powder diffraction data rules out the possibility that some of the europium might be located on titanium sites.

Keywords Ferroelectric · Mössbauer spectroscopy · Electron electric dipole moment

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1 Introduction

For many years people have searched for signs of permanent electric dipole moments (EDM) of particles such as electrons and neutrons, or diamagnetic atoms such as ^{199}Hg. If such EDM exist, the accompanying violation of time-reversal symmetry would imply CP-violation, through the CPT theorem which states that any Lorentz-invariant field theory must be invariant under the combined CPT symmetry. The Standard Model predicts vanishingly small EDM (10^{-42} e-cm for the electron, for example). The present experimental upper limit for the electron EDM is 1.6×10^{-27} e-cm which is already sufficient to rule out some supersymmetric extensions to the Standard Model.

One proposal to search for the electron EDM involves electric-field induced magnetization studies of the ferroelectric material $Eu_{0.5}Ba_{0.5}TiO_3$. This novel approach is predicted to yield an order of magnitude improvement in the EDM detection limit [1, 2]. The magnetic ferroelectric material $Eu_{0.5}Ba_{0.5}TiO_3$ forms the cubic perovskite structure (space group $Pm\overline{3}m$) at room temperature, and undergoes a ferroelectric transition at about 170 K. The magnetic ordering temperature is approximately 1.9 K.

Ferroelectric transitions are generally driven by relative displacements of ions and involve phonon mode softening. The mechanism of phonon mode softening was introduced by Cochran [3] and Anderson [4] in 1959/60. Its effect on a Mössbauer spectrum was proposed by Muzikar et al. [5] in 1963; the mode softening manifests itself as a decrease in the Mössbauer–Lamb recoil-free fraction (f-factor) due to the increasing vibrational amplitude. Therefore, a decrease in the spectral area is expected at the transition temperature. Such a dip was first observed in Fe-doped $BaTiO_3$ by Bhide and Multani in 1965 [6] and expanded to Fe-doped $PbTiO_3$ by Bhide and Hegde [7].

In this paper we concentrate on the 'materials' aspects of $Eu_{0.5}Ba_{0.5}TiO_3$ and in particular we demonstrate the effect of the phonon mode softening at the ferroelectric transition by studying the ^{151}Eu Mössbauer resonance. Here, the effect of the phonon softening is seen clearly in a primary component of the crystal phase, rather than at a dopant site.

2 Experimental methods

The $Eu_{0.5}Ba_{0.5}TiO_3$ samples were prepared by solid-state reaction of Eu_2O_3, TiO_2 and $BaTiO_3$ powders and a detailed description of the preparation technique can be found in [1]. Sample quality was monitored by x-ray powder diffraction on a Scintag PAD V diffractometer. ^{151}Eu transmission Mössbauer spectra were collected on a constant acceleration spectrometer using a 4 GBq $^{151}SmF_3$ source. The 21.6 keV γs were detected using a NaI(Tl) scintillation detector and the spectrometer's velocity scale was calibrated using ^{57}Co**Rh** and $\alpha-$Fe. All ^{151}Eu isomer shifts are quoted relative to the $^{151}SmF_3$ source. Low-temperature spectra were collected using a vibration-isolated closed-cycle refrigerator. The spectra were fitted with a pair of equal-linewidth Lorentzians (one for each of the Eu^{2+} and Eu^{3+} components) using a conventional non-linear least-squares minimisation routine.

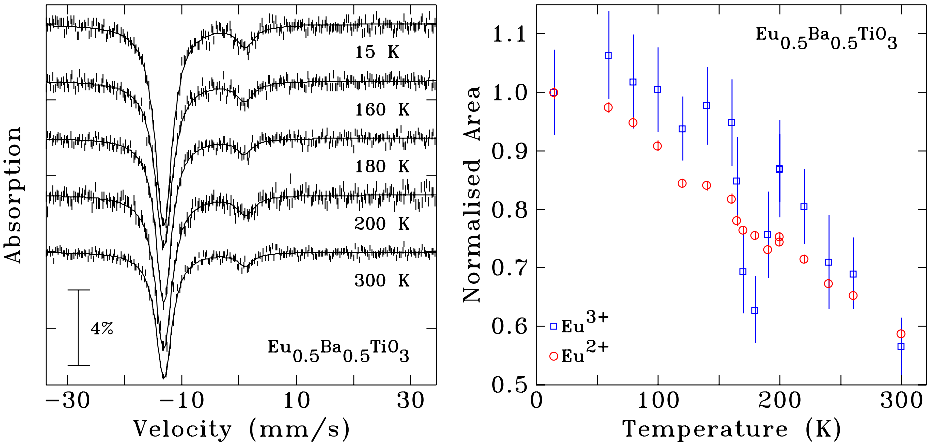
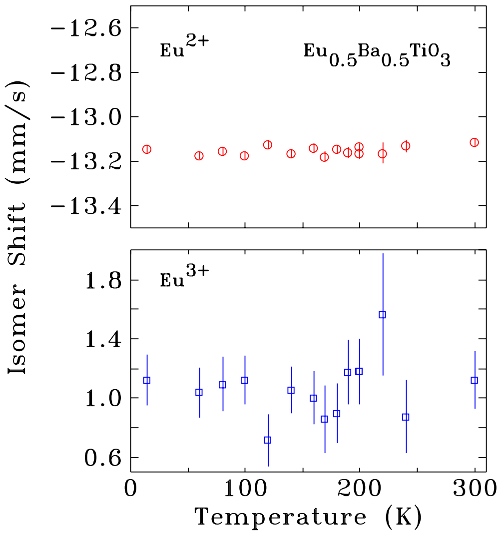


Fig. 1 *Left* ^{151}Eu Mössbauer spectra of $Eu_{0.5}Ba_{0.5}TiO_3$; *Right* normalized subspectral areas of the Eu^{2+} and Eu^{3+} Mössbauer components

Fig. 2 Temperature dependences of the Eu^{2+} (*top*) and Eu^{3+} (*bottom*) isomer shifts in the ^{151}Eu Mössbauer spectra of $Eu_{0.5}Ba_{0.5}TiO_3$



3 Results

In Fig. 1 we show the ^{151}Eu Mössbauer spectra of $Eu_{0.5}Ba_{0.5}TiO_3$ obtained over the temperature range 15–300 K. All spectra are paramagnetic and are dominated by the Eu^{2+} spectral component with an isomer shift of −13.12(1) mm/s at 300 K. In all spectra we observe a much smaller component with an isomer shift of +1.1(2) mm/s at 300 K, corresponding to Eu^{3+}. The relative subspectral areas of the Eu^{2+} and Eu^{3+} components at temperatures well below or well above the ferroelectric transition are 90(1)% and 10(1)%, respectively. Our initial assignment of this Eu^{3+} spectral component was to some unreacted Eu_2O_3 but, as we discuss below, this Eu^{3+} component is in fact localized within the $Eu_{0.5}Ba_{0.5}TiO_3$ phase itself.

In Fig. 1 we also show the normalized subspectral areas of the Eu^{2+} and Eu^{3+} components in the ^{151}Eu Mössbauer spectra of $Eu_{0.5}Ba_{0.5}TiO_3$. There is a clear dip in both signals at around 175 K which corresponds to the ferroelectric transition from the high-temperature cubic ($Pm\overline{3}m$) phase to the lower-temperature tetragonal (P4/mmm) phase. The fact that the Eu^{3+} component shows this pronounced dip is a clear indication that the Eu^{3+} is not due to some unreacted Eu_2O_3, which shows no such behaviour.

In Fig. 2 we show the temperature dependences of the isomer shifts of the Eu^{2+} and Eu^{3+} spectral components. These data show that there are no valence instabilities associated with the ferroelectric transition.

The temperature dependence of the f-factor shows a much stronger response in the Eu^{3+} component than in the Eu^{2+} one. Preliminary analysis of neutron powder diffraction data rules out the possibility that some of the europium might be located on titanium sites. Furthermore, we have not observed clear signs of any deviations from the nominal chemical stoichiometries. Thus, the origins of the enhanced phonon softening at the Eu^{3+} site remain unclear. One possible factor is the size of the Eu^{3+} ion which is about 15 % smaller than the Eu^{2+} ion: for example, the 8-coordinated Shannon radii are 1.066 Å and 1.25 Å, respectively [8]. The Eu ions substitute for the Ba^{2+} ions in $BaTiO_3$ and in the ideal cubic perovskite structure would be 12-coordinated. The distortion associated with the transition to the ferroelectric state reduces this coordination. The smaller Eu^{3+} ion presumably is subject to weaker bonding than the larger Eu^{2+} ion.

Finally, since the phonon mode softening at the ferroelectric transition in $Eu_{0.5}Ba_{0.5}TiO_3$ has such a marked effect on the Eu sites, this material provides an ideal system in which to exploit synchrotron–Mössbauer to study the behaviour of the local phonon density of states through the ferroelectric transition.

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