Lattice instabilities in bulk EuTiO$_3$

D. Bessas$^{1,2,†}$, K. Z. Rushchanskii$^3$, M. Kachlik$^4$, S. Disch$^{1,5}$, O. Gourdon$^{6,7}$, J. Bednarcik$^8$, K. Maca$^4$, I. Sergueev$^{1,8}$, S. Kamba$^9$, M. Ležaić$^3$ and R. P. Hermann$^{1,2}$

1Jülich Centre for Neutron Science JCNS and Peter Grünberg Institut PGI, JARA-FIT, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

2Faculté des Sciences, Université de Liège, B-4000 Liège, Belgium

†Present address: European Synchrotron Radiation Facility, F-38043, Grenoble, France

3Peter Grünberg Institut, Quanten-Theorie der Materialien, Forschungszentrum Jülich and JARA, D-52425 Jülich, Germany

4CEITEC Brno University of Technology, 61600, Brno, Czech Republic

5Institut Laue-Langevin, F-38042, Grenoble, France

6Neutron Scattering Science Division, Oak Ridge National Laboratory, TN 37831, Oak Ridge, United States

7Jülich Centre for Neutron Science JCNS, Oak Ridge National Laboratory, TN 37831, Oak Ridge, United States

8Deutsches Elektronen-Synchrotron, D-22607 Hamburg, Germany

9Institute of Physics ASCR, 18221, Prague, Czech Republic

Abstract

The phase purity and the lattice dynamics in bulk EuTiO$_3$ were investigated both microscopically, using X-ray and neutron diffraction, $^{151}$Eu-Mössbauer spectroscopy, and $^{151}$Eu nuclear inelastic scattering, and macroscopically using calorimetry, resonant ultrasound spectroscopy, and magnetometry. Furthermore, our investigations were corroborated by \textit{ab initio} theoretical studies. The perovskite sym-
metry, $\text{Pm}\bar{3}m$, is unstable at the $M$- and $R$- points of the Brillouin zone. The lattice instabilities are lifted when the structure relaxes in one of the symmetries: $I4/\text{mcm}$, $\text{Imma}$, $R\bar{3}c$ with relative relaxation energy around $-25$ meV. Intimate phase analysis confirmed phase purity of our ceramics. A prominent peak in the Eu specific density of phonon states at $11.5$ meV can be modeled in all candidate symmetries. A stiffening on heating around room temperature is indicative of a phase transition similar to the one observed in SrTiO$_3$, however, although previous studies reported the structural phase transition to tetragonal $I4/\text{mcm}$ phase our detailed sample purity analysis and thorough structural studies using complementary techniques did not confirm a direct phase transition. Instead, in the same temperature range, Eu delocalization is observed which might explain the lattice dynamical instabilities.

1 Introduction

Perovskites exhibit cubic symmetry at high temperature, with space group $\text{Pm}\bar{3}m$ and a large flexibility of site occupancy by a broad range of elements on the $A$ and $B$ sites \cite{1} and flexibility in oxygen stoichiometry on the $X$ site \cite{2}, indicated in the general chemical formula $ABX_{3+\delta}$. The oxygen in the perovskite unit cell form interconnected octahedra, the rotation of which are potentially responsible for distortions away from the cubic symmetry and structural transitions \cite{3}. Ba, Sr, and, to a lesser extent, Eu perovskite titanates are interesting owing to their ferroelectric properties and their potential applications in information technology. EuTiO$_3$ is an incipient ferroelectric perovskite, like SrTiO$_3$, with however magnetic cations on the $A$-site and it undergoes a transition to a G-type antiferromagnetic phase below $5.3$ K \cite{4,5}. Recently, ferroelectric instability in EuTiO$_3$ films \cite{6} under 1\% tensile stress was reported. However, in bulk EuTiO$_3$ the cubic $\text{Pm}\bar{3}m$ structure was till recently supposed to be stable down to LHe temperature \cite{7}. Only lately some hints of an antiferrodistortive phase transition to a tetragonal $I4/\text{mcm}$ phase were observed, but the critical temperature varied from $200$ to $282$ K \cite{8,9,10,11}. These results were consistently checked by Goian et al. \cite{12} and attributed to the sample quality.

Inelastic X-ray scattering on tiny single crystals was only very recently reported \cite{13} and shows that the antiferrodistortive phase transition cannot be of order - disordered type, as was proposed by Bussmann-Holder et al. \cite{8,14}, but is instead displacive with a soft mode at the $R$-point of the Brillouin zone. However, similar zone boundary phonon softening has been identified without the observation of a structural phase transition by Swainson et al. \cite{15} e.g. in relaxors.

In this study we present a detailed investigation of the phase purity, the crystallinity and the lattice dynamics in bulk polycrystalline EuTiO$_3$ using both microscopic and macroscopic measurements as well as theoretical calculations. We demonstrate that a
lattice instability associated with Eu anharmonic displacements appears close to room temperature.

2 Methods

2.1 Experimental Techniques

Phase pure EuTiO$_3$ polycrystalline samples were prepared using a stoichiometric ratio of precursors (Eu$_2$O$_3$ 99.99% and Ti$_2$O$_3$ 99.9%). The mixture was homogenised in a planetary ball mill, cold isostatically pressed at 300 MPa, and sintered in pure hydrogen at 1400 °C for 2 hours. The processing details are given elsewhere [16]. The sintered pellets had a relative density of 89%. All measurements were performed on ceramic pieces or powder taken from the same pellet.

The crystallographic phase purity and potential structural transitions were checked by temperature dependent powder diffraction between 10 and 300 K using high-energy synchrotron radiation, wavelength 0.142013 Å, at station 6-ID-D/APS. In order to extend the temperature range up to 400 K similar measurements were carried out with 0.20727 Å wavelength on the same sample at station P02.1/PETRAIII. The overall precision including sample size and detector pixel size was estimated using standard samples to $\Delta d/d \sim 5.0 \times 10^{-3}$ for measurements carried out at 6-ID-D and $\Delta d/d \sim 1.0 \times 10^{-2}$ for measurements carried out at P02.1. The atomic behaviour in EuTiO$_3$ was further studied by neutron diffraction. Europium is a strong neutron absorber [17], thus a thin homogeneous powder layer was prepared using 700 mg of EuTiO$_3$ and placed between thin vanadium foils (0.02 x 10 x 30 mm$^3$). Neutron scattering data were collected between 150 and 350 K using the time-of-flight, T.O.F., instrument POWGEN [18], with precision $\Delta d/d \sim 1.5 \times 10^{-3}$ at $d = 1$ Å, and between 10 and 300 K using the T.O.F. instrument NOMAD [19] at the Spallation Neutron Source. The neutron pair distribution function, PDF, analysis was carried out on the data obtain at NOMAD by Fourier transformation of the total scattering function [20].

The phase purity was further investigated using $^{151}$Eu-Mössbauer spectroscopy between 90 and 325 K on fine powder of EuTiO$_3$, 35 mg/cm$^2$, mixed with BN, using a calibrated spectrometer.

Heat capacity measurements were recorded in the Quantum Design cryostat (QD-PPMS) utilising the built-in calorimeter. Measurements of both the addenda and sample were performed at the same temperatures between 10 and 340 K with a 0.5 K point density in the region of interest. Every data point was measured three times and an average value was extracted.

The macroscopic lattice dynamics was probed by Resonant Ultrasound Spectroscopy (RUS) [21]. Temperature dependent spectra between 100 kHz and a few MHz were recorded on a shaped sample (2.5 x 2 x 1.5 mm$^3$) using an in-house spectrometer made
Figure 1: Rietveld refinement (black line) of a typical EuTiO$_3$ diffractogram (red points) and the corresponding refinement residuals (blue line) using: (a) synchrotron radiation at 300 K and (c) neutrons at 180 K. (b) The FWHM of certain reflections ($R_0$, $R_1$ and $R_2$) measured with two different instrumental resolutions (see text). Inset to (a) shows the temperature dependent lattice parameter (pointsize defines errorbars) in cubic symmetry.
with cylindrical Y-cut LiNbO\(_3\) 0.3 mm thick transducers (Ø 1.5 mm) inside a QD-PPMS.

Magnetic characterizations was carried out in a Cryogenics Ltd. measurement system using AC susceptibility measurements below 30 K (\(f = 20.4\) Hz, \(H_{dc} = 10\) G at \(H_{dc} = 0\) G) as well as DC susceptibility measurements (\(H_{dc}^{max} = 5\) kG, at \(T = 4.9\) K).

To support our macroscopical lattice dynamical characterization microscopic investigations based on nuclear inelastic scattering [22], NIS, of \(^{151}\)Eu in EuTiO\(_3\) were performed. Several spectra were recorded at 110, 210, 295 and 360 K in 16-bunch mode at the nuclear resonance station ID22N/ESRF [23] using a nested monochromator [24] providing 1.5 meV resolution.

### 2.2 Theoretical Techniques

The Eu specific density of phonon states, \(i.e.\) the spectral distribution of the Eu vibrational amplitude, for \(I_{4}/mcm\), \(Imma\) and \(R\overline{3}c\) structures were calculated using the PHON code [25] by integrating the eigenvectors and eigenvalues of the corresponding dynamical matrices over the Brillouin zone. We used a 30 x 30 x 30 \(q\)-point mesh and the experimental FWHM for Gaussian convolution. Details on the calculation of the dynamical matrices as well as the crystallographic parameters of the used structures are given in Ref. [26].

### 3 Results

#### 3.1 Microscopic Characterization

A typical X-ray diffractogram recorded on polycrystalline EuTiO\(_3\) is shown in Fig.1a. The \(Q\) range of our scattering data reached approximately 13 Å\(^{-1}\) using neutrons. A typical T.O.F. neutron diffractogram is given in Fig.1c. All observed reflections were identified in all possible symmetries. No peak splitting characteristic of structural phase transitions was observed in our temperature dependent measurements using both X-rays and neutrons. In order to account for any resolution limited satellite reflection the Full Width Half Maximum, FWHM, of all reflections was studied using a Lorentzian profile. The extracted FWHM of selected reflections between 10 and 400 K (indicated in Fig.1a by \(R_1 \equiv (3\ 1\ 0)\) in \(Pm\overline{3}m\) or \{(1\ 3\ 4),(1\ 2\ 8)\} in \(R\overline{3}c\) or \{(1\ 1\ 6), (3\ 3\ 2), (4\ 2\ 0)\} in \(I4/mcm\) or \{(0\ 6\ 4), (2\ 6\ 0), (0\ 2\ 12), (2\ 0\ 12), (6\ 2\ 0), (6\ 0\ 4)\} in \(Imma\) and \(R_2 \equiv (3\ 1\ 1)\) in \(Pm\overline{3}m\) or \{(0\ 4\ 2), (2\ 2\ 6), (0\ 2\ 10)\} in \(R\overline{3}c\) or \{(4\ 2\ 2), (2\ 0\ 6)\} in \(I4/mcm\) or \{(2\ 6\ 4), (2\ 2\ 12), (6\ 2\ 4)\} in \(Imma\) are shown in to Fig.1b. The FWHM of all the examined reflections which are supposed to split broadens upon cooling below \(\sim 300\) K. This is not the case for \(R_0 \equiv (1\ 0\ 0)\) in \(Pm\overline{3}m\) or \(0\ 1\ 2\) in \(R\overline{3}c\) which shows temperature independent FWHM. Although the observation of
Figure 2: Temperature dependent $^{151}$Eu-Mossbauer spectra measured on EuTiO$_3$ powder (black points) and the corresponding two component model (black line). The expected isomer shift relative to EuF$_3$ is indicated with tics. The inset shows the temperature dependent Lamb–Mössbauer factor, $f_{LM}$, of the majority phase, Eu(II), extracted from the spectra and the associated Debye model (black dashed line).
temperature dependent FWHM in some particular reflections might be indicating departure from cubic symmetry, new reflections were not observed in our diffractogram. The diffraction data were further refined with Fullprof [27] using the Rietveld method. A typical refinement, with \( R_{wp} = 8.3\% \), is shown in Fig. 1a. The inset to Fig. 1a shows the extracted lattice parameter in cubic symmetry vs temperature. The extracted lattice parameter is in excellent agreement with reference data [7]. Linear thermal expansion is observed between 100 and 300 K. The calculated volume thermal expansion coefficient, \( \alpha_V \), after fitting the lattice parameter with a linear function normalised to the lattice parameter at 300 K is \( \alpha_V = 9.9(1) \times 10^{-6} \text{ K}^{-1} \).

Minor deviations from linearity are observed between 200 and 270 K which might support the claim of instabilities in this region. However, no sign for a phase transition is observed.

The neutron diffraction data obtained at POWGEN were further refined with JANA2006 [28] using the Rietveld method resulting in \( R_{wp} = 7.4\% \). The extracted lattice parameter in cubic symmetry is in excellent agreement with the one extracted using X-rays. In addition, the atomic displacement parameters, ADP, of Eu, Ti and O at 180 K extracted in the harmonic approximation are 21.0(8), 7.3(5) and 7.5(5) (x10^{-3} \text{ Å}^2) respectively and do not show any substantial irregularity vs temperature. Note that in isostructural SrTiO\(_3\) the atomic displacements of Sr and Ti in the antiferrodistortive phase are comparable [29] to that of Eu in EuTiO\(_3\).

Typical Mössbauer spectra between 90 and 325 K are given in Fig. 2. The data were fitted with a two component model, the second component contributing by less than 1(1)\% to the total area. The extracted isomer shift for the major component is \(-12.45(5) \text{ mm/s} \) relative to EuF\(_3\), an isomer shift indicative of Eu(II). Thus, the sample contained purely divalent Eu. The upper limit of Eu(III) which might escape detection is 1%. A Debye temperature of 295(5) K, was calculated within the Debye approximation [30] from the temperature dependent Lamb - Mössbauer factor, \( f_{LM} \). In contrast to the prediction by Bussmann-Holder et al. [8] no line splitting or broadening was found in our temperature dependent Mössbauer spectra.

Pair Distribution Function analysis (PDF) probes local disorder in crystalline materials [32, 33]. In contrast to Rietveld refinements, the diffuse scattering and other background contributions are of crucial importance because a Fourier transformation is applied to the total scattering function. In this case, the large neutron absorption combined with the time-of-flight instrument prevent accurate background subtraction and produces oscillations in the extracted PDF thus in this study background contributions are treated phenomenologically. The refinement was conducted using PDFgui [34] between 2.5 and 50 Å, see Fig. 3a. Within the limited precision of our extracted PDF no clear change with temperature in the interatomic distances of oxygen with europium is observed, see Fig. 3b.

Several experimental methods for probing lattice dynamics exist. However, ac-
Figure 3: (a) Pair Distribution Function analysis (PDF) of neutron scattering data, $Q = 50 \text{ Å}$, (black points), at 300 K, and the corresponding refinement (red line). The refinement residual (blue line) is given in the same scale and represents a fair refinement. (b) shows a close up in the temperature dependent PDF analysis (black lines) and a typical PDF analysis refinement (red line) around the first nearest neighbor distances regime, indicated with dashed lines. Note that at a lattice parameter distance, 3.905 Å
Figure 4: (a) The Eu specific density of phonon states in EuTiO$_3$ at 210 K (black tics) and 360 K (red line-tics) measured using NIS, typical errorbar is given, and our theoretical spectra for different structures[26]. (b) Heat capacity data between 10 and 340 K measured on EuTiO$_3$ using calorimetry (pointsize defines errorbar), line between points is guide to the eye. (c) The first 5 meV of the reduced $^{151}$Eu projected density of phonon states, $g(E)/E^2$, and the related Debye levels (dashed lines). (d) The real part, Re$Y_{[100]}^{[100]}$, and the imaginary part, Im$Y_{[100]}^{[100]}$, of the complex Young’s modulus in SrTiO$_3$ obtained from Ref. [31]. (f) Speed of sound extracted from RUS (black points), pointsize defines errorbar, and the corresponding extracted from NIS (red circles) at 210, 300 and 360 K. (g) The inverse quality factor of the resonance at 590 kHz between 200 and 370 K.
cess to the full Density of Phonon States (DPS), $g(E)$, is feasible only by inelastic neutron [35] or X-ray scattering [36]. In this work, nuclear resonance inelastic measurements which requires the existence of Mössbauer active isotope and synchrotron radiation were carried out. The raw spectra were treated using a modified version [37] of the program DOS [38]. The $^{151}\text{Eu}$-specific density of phonon states [39], DPS, was extracted between 0 and 24 meV, see Fig. 4a. A single peak around 11.5 meV is observed, in agreement with our first principles calculations in all possible symmetries. No resolvable change has been observed in the $^{151}\text{Eu}$ DPS between 210 and 360 K. The $^{151}\text{Eu}$ mean force constant can be extracted from our data using the expression 

$$
\langle F_i \rangle = M_i \int_0^\infty g(E)E^2dE/\hbar^2,
$$

where $M_i$ is the mass of the resonant isotope. Between 110 and 360 K the extracted $^{151}\text{Eu}$ mean force constant ranges from 78 to 70 N/m.

From our NIS data the $^{151}\text{Eu}$ ADP, $\langle u^2 \rangle$, were extracted using 

$$
\langle u^2 \rangle = -ln f_L / k^2,
$$

where $k$ is the wavenumber of the resonant photons. $\langle u^2 \rangle$ are in fair agreement with those extracted from neutron diffraction due to incoherent - coherent origin, respectively [40].

In the long wavelength limit, in this work assumed below 4 meV, the average speed of sound, $\nu_s$, can be extracted from the DPS using: 

$$
\lim_{E \to 0} \frac{g(E)}{E^2} = \frac{M_i^2}{2\pi \rho \nu_s^3},
$$

where $M_i$ is the isotopic mass and $\rho$ is the mass density. A linear fit of the $g(E)/E^2$, below 4 meV, between 110 and 360 K is given in Fig. 4c. The extracted speed of sound is included in the same figure.

### 3.2 Macroscopic Characterization

In order to verify claims of a striking phase transition observed in the heat capacity, $C_p$, of EuTiO$_3$ [8, 42] the same cryostat, Quantum Design, was used. Special attention was taken on the thermal coupling between the measuring platform and the sample [43]. Every data point was measured three times and an average value has been extracted. The averaged data are shown in Fig. 4b. The measured heat capacity in EuTiO$_3$ reveals no evidence of a structural phase transition in contrast with what has been observed in Ref. [8, 42] and using similar techniques in SrTiO$_3$ [44]. Hence, we conclude that the observation reported in Ref. [8, 42] is related either to sample purity or inadequate background subtraction.

The isotropic elastic tensor, $C_{11}$ and $C_{44}$, was extracted from the spectrum of resonant ultrasound spectroscopy and the bulk, $B_{295\,\text{K}} = 125$ GPa, and shear, $G_{295\,\text{K}} = 76$ GPa, moduli were calculated. The extracted polycrystal shear wave speed, $\nu_s$, is shown in Fig. 4f. In Fig. 4g the inverse quality factor, $Q_i$ [45], of a typical mechanical resonance at 590 kHz is shown. The average speed of sound calculated from the isotropic elastic tensor indicates 25% hardening at 300 K relative to 100 K. Similar behaviour was observed on a second sample from the same batch.

In our magnetic characterization measurements, see Fig. 5, a prominent peak at $T = 5.2(1)$ K appears in magnetic susceptibility. No other magnetic transitions were
identified below 30 K. Below the observed transition, at 4.9 K, dc magnetization was measured up to $\mu_0 H_{dc} = 5$ T and neither a hysteretical behavior nor a ferromagnetic contribution were observed.

3.3 Theoretical Investigations

Our first-principle calculations [26] on EuTiO$_3$ show that the $Pm3m$ symmetry is unstable at the $M$- and $R$- points of the Brillouin zone with respect to the rotation of the oxygen octahedra. The lattice instabilities are removed when the structure relaxes in one of three symmetries: tetragonal ($I4/mcm$), orthorhombic ($Imma$) or rhombohedral ($R\bar{3}c$) all with relative relaxation energies between $-25$ and $-27$ meV to the cubic symmetry. The energy difference between the distorted structures is very small and allows in fact polymorphism. The Eu specific density of phonon states in all calculated structures is in excellent agreement with the measured one, see Fig. 4a. We note that although in $Imma$ phase a Eu atomic displacement is allowed and its calculated size [26] is 0.012 Å.

4 Discussion

Although no obvious structural instability was identified by diffraction or calorimetry, a prominent acoustical stiffening upon heating is nevertheless observed between 100 and 300 K, a stiffening which is corroborated by a peak in the quality factor, $Q_i$, at 290 K. In the same temperature range the diffraction peaks which are suppose to split upon phase transition broaden on cooling, see Fig. 1. Above 310 K the FWHM of the same reflections as well as the speed of sound are found to be essentially temperature independent. A similar behaviour was observed in the real and imaginary part of Young’s modulus around 100 K in SrTiO$_3$ [31], see Fig. 4d and Fig. 4e, however, in SrTiO$_3$ a well known structural transition around 100 K takes place [46]. Based on ultrasonic experiments Rehwald [47] qualifies the observed phase transition in SrTiO$_3$ as a second order and not as order-disorder but as soft mode type. In order to understand the nature of the acoustical stiffening in EuTiO$_3$ which appears rather similar to the one observed in SrTiO$_3$ detailed structural and phase purity analysis was carried out.

Divalent Eu based titanium compounds, such as EuTiO$_3$, have been investigated extensively by McGuire et al. [48] owing to their remarkable variety in magnetic properties. Among them, pyrochlore compound Eu$_3$Ti$_2$O$_7$ and Eu$_2$TiO$_4$ perovskite are impurity candidates in any EuTiO$_3$ sample. According to literature [49], both compounds show ferromagnetic transitions around 8.7 ± 0.3 K. However, in our magnetization data, see Fig. 5, neither ferromagnetic transition appeared around 9 K nor is a ferromagnetic contribution present in the $M - H$ curve below the antiferromagnetic transition temperature. As a result, within our instrumental resolution and with the combined use
Figure 5: Temperature dependence of the ac magnetic susceptibility measured on cooling in sample in EuTiO$_3$ using an oscillating magnetic field with frequency $f = 20.4$ Hz amplitude $H_{ac} = 10$ G at $H_{dc} = 0$ G. Inset shows a $M - H$ curve measured on the same sample at 4.9 K with maximum applied magnetic field of $H_{dc} = 50$ kG.
of several characterization methods, neither Eu$_3$Ti$_2$O$_7$ nor Eu$_2$TiO$_4$ are present in our sample. Thus combining the results of magnetic characterization with the Mössbauer spectroscopy our sample properties are consistent with the reported antiferromagnetic properties of EuTiO$_3$\textsuperscript{[49]} and preclude other europium titanates\textsuperscript{[50, 51, 52]}. Mössbauer spectroscopy and nuclear inelastic spectroscopy are complementary methods since they are based on the same principle. This is illustrated once more by the fact that the NIS extracted $f_{LM}$ agrees within 95\% with the one extracted by Mössbauer spectroscopy. From the long wavelength limit, below 4 meV, of the DPS the speed of sound, $\nu_s$, was calculated. The DPS extracted speed of sound indicates hardening of EuTiO$_3$ versus temperature, as observed also using RUS, see Fig. 4f. Both microscopic and macroscopic measurements are in good agreement. The 10\% deviation at 210 K is reproducible and can be associated with isothermal speed of sound measured via scattering, and adiabatic sound measured with RUS. As a result, the increase in speed of sound upon heating is verified both by microscopic and macroscopic techniques and is in contrast to the usual softening of elastic constants upon heating\textsuperscript{[53]} confirming lattice instability of EuTiO$_3$ between 100 and 300 K. The temperature behaviour of the adiabatic speed of sound is not consistent with an order - disorder transition\textsuperscript{[47]}. Pair Distribution Function analysis (PDF) probes local disorder in crystalline materials\textsuperscript{[32, 33]}. The PDF can be derived either from X-ray or neutron total scattering data with advantages and disadvantages described extensively by Egami and Billinge\textsuperscript{[20]}. In this study we carried out PDF analysis on our neutron data because if there was any potential oxygen displacement it would be more visible using neutrons due to the enhanced neutron cross section with respect to X-rays. The main information extracted from PDF without further modeling is the interatomic distances, see Fig.3b. Ti has a negative coherent scattering length which results in negative peaks for the $A$,$X$-Ti correlations, where $A$ and $X$ are the perovskite sites. Europium neutron absorption introduces anomalous background in the total scattering as function of the scattering angle. Hence, the Fourier transformation of the total scattering function might introduce artifacts in the PDF which cannot be modeled. Fig.3a shows the room temperature PDF of EuTiO$_3$. Although all interatomic distances were modelled sucessfully and the extracted parameters (lattice parameters, atomic displacement parameters) agree with those extracted from Rietveld refinement, the goodness of fit is relatively poor. In case there was a pronounced phase transition, the interatomic distance between Eu - Eu, Ti - Ti and O - O it would change and a doublet instead of single peak is expected at the corresponding interatomic distance. However, the highlighted part of Fig.3b does not show any consistent variation. The expected Eu - Eu correlation peak, and similarly the Ti - Ti and O - O, is not observed probably because the variations in PDF introduced by Eu absorption was not modelled correctly.

Although absolute values of ADP extracted using coherent techniques such as diffraction might be affected by occupancies, relative changes of the ADP extracted
Figure 6: (a) The atomic displacement parameters, ADP, extracted in the harmonic approximation from neutron diffraction, typical errorbar is given. (b) Probability density function, p.d.f, distribution of the Eu-atom in the \(ab\) plane at 180 K. (c) The effective one-particle potential of the Eu atom along the \(a\) direction \((y = 0)\) at 320, 295, 250 and 180 K obtained from crystallographic structure analysis and the typical errorbar. (d) The potential barrier, \(V_0\), and the displacement from equilibrium position, \(2d\), (dashed line is guide to the eye) extracted from the potential given in (c).
Table 1: Temperature dependent anharmonic refined parameters $D_{ijkl}^{GC}(r)$ of Eu atom in EuTiO$_3$ refined using the Gram-Charlier expansion

| Temperature (K) | $D_{1111}^{GC}(r)$ | $D_{1122}^{GC}(r)$ | $D_{1133}^{GC}(r)$ | $D_{2222}^{GC}(r)$ |
|-----------------|----------------------|----------------------|----------------------|----------------------|
| 320             | -426.0(1)            | -65.7(8)             | -375.6(1)            | -67.5(6)             |
| 295             | -375.8(2)            | -67.5(6)             | -329.8(1)            | -69.2(7)             |
| 250             | -329.8(2)            | -67.5(6)             | -88.7(1)             | -35.1(4)             |
| 180             | -88.7(1)             | -35.1(4)             |                     |                      |

from such measurements are still valid. Although all extracted ADP have smooth dependence on temperature the Eu ADP is large as compared to Ti and O, see Fig. 6a. Hence, a Fourier map study in the vicinity of Eu was carried out. The Gram-Charlier expansion of anharmonic atomic displacement parameters is extensively described in Ref. [54] and has been followed in several cases of perovskite structure [55, 56] with reported anharmonic atomic displacements. In this study, the Eu atomic displacement parameters extracted from neutron diffraction assuming cubic symmetry, $Pm3m$, was modeled using a Gram-Charlier expansion of the probability density function, p.d.f., $p_{GC}^{Eu}$, up to fourth-rank tensor[57] given in Eq. 1.

$$p_{GC}^{Eu}(r) = p_{Eu}^{harm}(r)[1 + \frac{1}{4}D_{ijkl}^{GC}(r)H_{ijkl}(r)]$$ (1)

where $r$ is the atomic displacement vector relative to the equilibrium position, $H_{ijkl}(r)$ is the Hermite polynomial of fourth order and $D_{ijkl}^{GC}(r)$ are anharmonic refined parameters (the third-order cumulants, $C_{ijkl}^{GC}(r)$ are zero, based on the site symmetry). The use of a fourth order Gram-Charlier expansion [54] for the Eu ADP improves the refinement. A reduction of the reliability factor from 5.03% to 4.07% just by adding a single parameter $D_{1111}^{GC}(r)$ has been observed. The refined Eu anharmonic parameters $D_{ijkl}^{GC}(r)$ at 110, 210, 295 and 360 K are given in the Table 1. Indeed, the Gram-Charlier tensor is following the symmetry restriction and therefore for the Eu at $(0, 0, 0)$; $C_{ijkl}^{GC}(r)$ are zero and $D_{ijkl}^{GC}(r)$ are non zero only for $D_{1111}^{GC}(r) = D_{2222}^{GC}(r) = D_{3333}^{GC}(r)$ and $D_{1133}^{GC}(r) = D_{1122}^{GC}(r) = D_{1144}^{GC}(r) = D_{2233}^{GC}(r)$. To justify the existence of such anharmonic behavior on the Eu site similar treatment has been attempted on the Ti and O sites. No major refinement improvement has been observed and thus we have no evidence for strong anharmonic behavior on the Ti and O sites. In Fig.6b the europium p.d.f. after final refinement at 180 K is illustrated. Eu exhibits off-centering in [1 0 0] and [0 1 0] directions (and equivalently in the [0 0 1] direction) with significant residual probability density in the azimuthal direction. The effective one-particle atomic potential, $V(r)$, is related to the p.d.f. by:

$$V(r) = -k_B T \ln \left[ \frac{p_{Eu}^{GC}(r)}{p_{Eu}^{GC}(r_0)} \right]$$ (2)

where $k_B$ is the Boltzmann constant and $T$ is temperature. In Fig.6 a section of the
Eu one-particle potential extracted according to the Eq. 2 is depicted along the [1 0 0] direction. These sections reveal that Eu exhibits temperature dependent off-centering, see Fig.6d, with \( d \sim 0.04 \text{ Å} \) at 180 K. In addition, the potential barrier along the azimuthal direction flattens well before 295 K, whereas at 250 K a double well potential is already formed. Note that this is the same temperature region in which specific diffraction peaks, see Fig. 1, start to broaden upon cooling. Above 295 K, the Eu p.d.f forms a plateau. An analogous double-well potential for EuTiO\(_3\) was suggested theoretically by Bettis et al. [14] although for oxygen displacement.

The plateau in the p.d.f. indicates increased Eu anharmonicity. In order to quantify anharmonicity, we estimated using our macroscopic measurements of \( C_p \), \( \alpha_V \), \( B \) and the Grüneisen rule [58] the Grüneisen parameter. Our estimation of \( \gamma \) at 290 K is, 1.3(1), in the same range with typical metallic compounds, \( \gamma \approx 2 \). To elucidate the impact of the Grüneisen parameter on our measured DPS we used the vibrational frequency definition of the Grüneisen parameter, \( \gamma = -\frac{d \ln E}{d \ln V} \), which relates the change in phonon mode energy to the change in volume. The estimated phonon mode energy shift, between 110 and 360 K using our measured \( \frac{dV}{V} \sim 0.0025 \) and our extracted average Grüneisen parameter of \( \gamma = 1.3 \) results in \( \frac{\delta E}{E} \sim 0.004 \). Therefore, the prominent peak, around 11 meV will not shift due to anharmonicity by more than 0.04 meV. Such energy mode shift is currently resolution limited.

EuTiO\(_3\) is an incipient ferroelectric, which means that its lattice is close to a ferroelectric instability at low temperatures. Note that theoretical calculations[26] indicate that the Eu displacement from its high-symmetry position is possible in tilted structures, e.g. Imma, however, this displacement is static. Significant dynamical displacement of Eu was observed in cubic \( Pn\bar{3}m \) structure even for the low-energy optical mode TO1, which eigenvector constitutes 37% of Last mode and 60% of the Slater, see Ref. [26]. This observation was used to design ferroelectric (Eu,Ba)TiO\(_3\) ceramics with significant off-centering on the magnetic cation site [59]. Also magnetoelectric coupling in EuTiO\(_3\) is exceptionally high [60] due to strong contribution of magnetic Eu cation in low energy polar mode. Note that in other multiferroics non-magnetic ions are displaced, e.g. Bi in BiFeO\(_3\) or Y in YMnO\(_3\), therefore the magnetoelectric coupling is usually smaller in such materials. Microscopic origin of the mixing character of the low-energy polar mode in cubic EuTiO\(_3\) is the coupling of the 4f orbitals of Eu\(^{2+}\) with the 3d states of nonmagnetic Ti\(^{4+}\) [61]. The influence of this coupling on the lattice instabilities of EuTiO\(_3\) was recently studied by Birol and Fennie [62]. It was found that partial occupation of the d-states on Ti due to hybridization drives EuTiO\(_3\) away from ferroelectric instability. This conclusion is compatible with results of Ref. [26], where it was shown that increasing volume of cubic EuTiO\(_3\), i.e. decreasing f-d hybridization, turns the low-energy mode to be unstable, with Slater type atomic displacement. Nevertheless, it is still not clear what is the effect of the oxygen vacancy on the structural stability of EuTiO\(_3\). Recently, it was shown [63] that doping
EuTiO₃ by N favors the tilted Pnma structure also at high temperatures. By means of hybrid functional calculations of electronic structure it was shown that the presence of impurities as well as the tilting of oxygen octahedra lead to delocalization of the Eu f-states, which modifies f-d coupling between A and B sites and, therefore, changes the lattice stability conditions. Note, that Pnma is subgroup of the Imma considered in Ref. [26], and is the one with off-centered Eu position. Thus, this particular field is still open to research and further theoretical and experimental studies are yet to come which will clarify the microscopic origin of the observed Eu shift in EuTiO₃.

The lattice dynamics in EuTiO₃ resembles that of SrTiO₃, the atomic delocalization in phase change materials [64] as well as the lattice dynamics in PbTe [65, 66]. In such cases the associated potential energy is considered as a multi-valley surface with drastical impact on thermal conductivity [67]. The observed phenomenon resembles rattling between minima in the potential energy and could be harnessed to lower the lattice thermal conductivity.

5 Conclusion

In summary, the combination of the extracted speed of sound by RUS and NIS, the Gram - Charlier expansion of Eu atomic displacements based on neutron diffraction and the feedback from theoretical studies based on ab initio calculations provides evidence for europium delocalization which originate in a lattice instabilities in the system. Short range coexistence of crystallographic phases with candidate symmetries Imma, R3m and I4/mcm in EuTiO₃ might be related to the fact that Eu delocalization does not lead to a structural transition. Experimental studies under high pressure on phase pure EuTiO₃ single crystals or thermal diffuse scattering experiments using synchrotron radiation might shed further light on this scenario. In addition, according to theoretical calculations a Eu atomic displacement is allowed in the Imma phase and its calculated size [26], 0.012 Å, corresponds roughly to the one measured in our experiment, however, phase transition with long range order is not observed. Reasonable scenarios might be nucleation of nanoclusters with Imma symmetry and different distortion direction which fail to extend to a reasonable corellation length or dynamical fluctuation of the distortion. Measurements of acoustic emission as it was presented [68] on BaTiO₃ might clarify this scenario. Similar atomic off-centering has been observed in a series of ferroelectric compounds such as Pb(Zr,Ti)O₃ and Pb(Mg₁/₃Nb₂/₃)O₃ [69].
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