

# Elastic constants and high-pressure structural transitions in lanthanum monochalcogenides from experiment and theory

G. Vaitheeswaran,<sup>1,\*</sup> V. Kanchana,<sup>1</sup> S. Heathman,<sup>2</sup> M. Idiri,<sup>2</sup> T. Le Bihan,<sup>3</sup> A. Svane,<sup>4</sup> A. Delin,<sup>1</sup> and B. Johansson<sup>1,5</sup>

<sup>1</sup>*Applied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology, Brinellvägen 23, 100 44 Stockholm, Sweden*

<sup>2</sup>*European Commission, JRC, Institute for Transuranium Elements, Postfach 2340, D-76125 Karlsruhe, Germany*

<sup>3</sup>*European Synchrotron Radiation Facility, Boîte Postale 220, F-38043 Grenoble Cedex, France*

<sup>4</sup>*Department of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark*

<sup>5</sup>*Condensed Matter Theory Group, Department of Physics, Uppsala University, P.O. Box 530, SE-751 21 Uppsala, Sweden*

(Received 23 January 2007; published 18 May 2007)

The high-pressure structural behavior of lanthanum monochalcogenides is investigated by theory and experiment. Theory comprises density-functional calculations of LaS, LaSe, and LaTe with the general gradient approximation for exchange and correlation effects, as implemented within the full-potential linear muffin-tin orbital method. The experimental studies consist of high-pressure angle dispersive x-ray-diffraction investigations of LaS and LaSe up to a maximum pressure of 41 GPa. A structural phase transition from the NaCl-type to CsCl-type crystal structure is found to occur in all cases. The experimental transition pressures are 27–28 and 19 GPa for LaS and LaSe, respectively, while the calculated transition pressures are 29, 21, and 10 GPa for LaS, LaSe, and LaTe, respectively. The calculated ground-state properties such as equilibrium lattice constant, bulk modulus and its pressure derivative, and Debye temperatures are in good agreement with experimental results. Elastic constants are predicted from the calculations.

DOI: [10.1103/PhysRevB.75.184108](https://doi.org/10.1103/PhysRevB.75.184108)

PACS number(s): 61.50.Ks, 71.15.Nc, 62.20.Dc, 71.20.Gj

## I. INTRODUCTION

The lanthanum monochalcogenides belong to the wide class of binary rare-earth monochalcogenides with the NaCl-type structure, which has been intensively studied because of their interesting physical properties including complex magnetic structures, pressure induced insulator-metal transitions, anomalous valence fluctuations, and unusual Fermi surface properties.<sup>1,2</sup> The trivalent lanthanum monochalcogenides are superconductors near 1 K, and the superconducting transition temperature as well as the electronic specific-heat coefficient increases from the monosulfide to the monotelluride, whereas the Debye temperature decreases from LaS to LaTe.<sup>3</sup>

In this work, we explore the high-pressure behavior of the La chalcogenides by experiment and theory. High-pressure x-ray-diffraction experiments are conducted on LaS and LaSe to obtain equations of states including discontinuous structural transitions from the NaCl structure (space group  $Fm\bar{3}m$ ,  $Z=1$ , also called the  $B1$  structure in the following) to the CsCl structure (space group  $Pm\bar{3}m$ ,  $Z=4$ , also termed the  $B2$  structure in the following). Density-functional calculations are performed to compare basic theoretical predictions with the measurements. The present experimental study of LaS extends our previous study on  $U_xLa_{1-x}S$  compounds.<sup>4</sup> For LaSe, no high-pressure results have been reported previously, while high-pressure experiments on LaTe report a structural transition from  $B1$  to  $B2$  at around 7 GPa.<sup>5</sup>

A second objective of the present work is to investigate the elastic properties of the lanthanum chalcogenides, for which there are no experimental results available. Elastic constants are derived from total energy variations with applied strains. We compare our results with recent theoretical work<sup>6</sup> and find good agreement.

The systematics of the electronic band structure through the lanthanum and cerium chalcogenide series was studied with angle-resolved photoemission spectroscopy.<sup>7,8</sup> The Fermi-surface properties of lanthanum monochalcogenides have been studied by de Haas–van Alphen effect measurements.<sup>9,10</sup> From the theoretical side, the energy-band structure, superconductivity, surface electronic structure, optical and magneto-optical spectra, as well as structural stability of lanthanum monochalcogenides have been investigated by several authors using the local spin-density approximation (LSDA) as well as the LSDA+U approximation.<sup>11–17</sup> A few papers also focused on the calculation of second and third order elastic constants using the short-range repulsive potential method.<sup>18–20</sup> A few experimental studies such as point contact spectroscopy,<sup>21</sup> reflectivity,<sup>22</sup> and phonon spectra<sup>23</sup> have been reported for LaS. The magneto-optical properties of lanthanum chalcogenides have been investigated experimentally,<sup>24–26</sup> where a nonzero Kerr effect could be observed in these Pauli paramagnets by applying an external magnetic field.

The rest of the paper is organized as follows. In Sec. II we discuss the computational and experimental details of our work. The calculated ground-state properties, elastic constants, as well as the experimental and theoretical results for the high-pressure behavior and structural transitions are presented in Sec. III, and the conclusions are given in Sec. IV.

## II. COMPUTATIONAL AND EXPERIMENTAL DETAILS

### A. Electronic structure method

In this work, we have used the all-electron full-potential linear muffin-tin orbital (LMTO) method<sup>27</sup> to calculate the

TABLE I. Calculated lattice constants in Å, bulk modulus in GPa, and its pressure derivative  $B'$  of the lanthanum monochalcogenides in the  $B1$  structure.

Compound		Lattice constant	Bulk modulus	$B'$
LaS	Expt., this work	5.852	89(3), 83.6 <sup>a</sup>	6.5(4)
	Theory, this work	5.873	87.8	3.95
	Other theory	5.812, <sup>b</sup> 5.773, <sup>c</sup> 5.727, <sup>d</sup> 5.895 <sup>c</sup>	97.74, <sup>b</sup> 107, <sup>d</sup> 81.53 <sup>e</sup>	4.67 <sup>e</sup>
LaSe	Expt., this work	6.067	74(2)	4.7(3)
	Theory, this work	6.091	74.8	4.12
	Other theory	5.957, <sup>d</sup> 6.126 <sup>e</sup>	97.74, <sup>d</sup> 68.40 <sup>e</sup>	4.28 <sup>e</sup>
LaTe	Expt.	6.435 <sup>f</sup>	60.6(2.0), <sup>g</sup> 55 <sup>h</sup>	
	Theory, this work	6.470	59.4	4.12
	Other theory	6.255, <sup>d</sup> 6.512 <sup>e</sup>	74.02, <sup>d</sup> 55.34 <sup>e</sup>	4.96 <sup>e</sup>

<sup>a</sup>Reference 35.

<sup>b</sup>Reference 12.

<sup>c</sup>Reference 14.

<sup>d</sup>Reference 16.

<sup>e</sup>Reference 6.

<sup>f</sup>Reference 10.

<sup>g</sup>Reference 36.

<sup>h</sup>Reference 2.

total energies and the basic ground state properties. Here, the crystal is divided into two regions: nonoverlapping muffin-tin spheres surrounding each atom and the interstitial region between the spheres. We used a double  $\kappa$  *spdf* LMTO basis (each radial function within the spheres is matched to a Hankel function in the interstitial region) for describing the valence bands. The following basis set was used in the calculations: La( $5s, 6s, 5p, 5d, 4f$ ), S( $3s, 3p, 3d$ ), Se( $4s, 4p, 3d, 4d$ ), and Te( $5s, 5p, 4d, 5d$ ). The exchange-correlation potential was calculated within the generalized gradient approximation (GGA) scheme.<sup>28</sup> The charge density and potential inside the muffin-tin spheres were expanded in terms of spherical harmonics up to  $l_{\max}=6$ , while in the interstitial region, they were expanded in plane waves, with 6566 (energy up to 109.80 Ry) waves being included in the calculation. Total energies were calculated as a function of volume, for a (18 18 18)  $k$  mesh, corresponding to 195  $k$  vectors in the irreducible wedge of the Brillouin zone, and the results fitted to the Birch equation of state<sup>29</sup> to obtain the ground-state properties.

The elastic constants were obtained from the variation of the total energy under volume-conserving strains, as outlined in Ref. 30.

## B. Experimental details

Experiments were carried out at the European Synchrotron Radiation Facility (ESRF), on the ID30 beamline dedicated to high pressure diffraction experiments, in the angular dispersive mode, using a double focused monochromatic beam at  $\lambda=0.3738$  Å. Loading of LaS and LaSe powders were performed in Le Toullec-type diamond-anvil cells, using nitrogen, argon, or silicone oil as the pressure transmitting media. The pressure inside the cell was determined via the ruby fluorescence method<sup>31</sup> from a small ruby ball mounted alongside the LaX sample. The sample to detector distance was calibrated before each set of experiments by means of a standard silicon powder sample. Diffraction images were captured with a FastScan<sup>32</sup> image plate detector and processed using the ESRF FIT2D program<sup>33</sup> to provide

TABLE II. Calculated elastic constants, shear modulus  $G$ , Young's modulus  $E$  (all given in GPa), and Poisson's ratio  $\nu$  for lanthanum monochalcogenides in the  $B1$  structure at the theoretical equilibrium volume. For comparison, results of LAPW calculations (Ref. 6) and experimental results for YS (Ref. 40) are included.

Compound	$C_{11}$	$C_{12}$	$C_{44}$	$G$	$E$	$\nu$	
LaS	227.9	18.0	22.2	55.3	137.2	0.240	Present
	234	23	25	46.6	117.8	0.26	LAPW
YS	250	20	30				Expt.
LaSe	201.6	11.4	15.7	47.5	117.5	0.238	Present
	203	21	22	40.6	102.5	0.26	LAPW
LaTe	158.7	9.7	7.9	34.5	86.8	0.256	Present
	171	12	8	24.6	64.1	0.30	LAPW

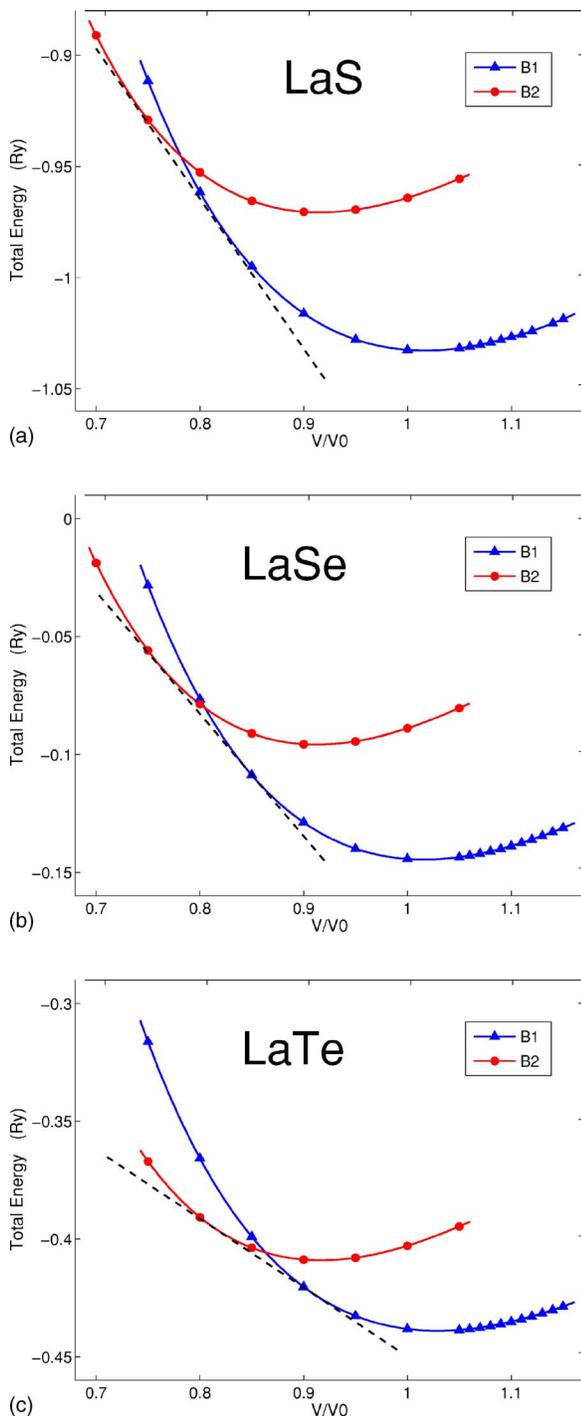


FIG. 1. (Color online) Calculated total energy vs relative volume for (a) LaS, (b) LaSe, and (c) LaTe in the B1 and B2 structures. The common tangents mark the structural B1  $\rightarrow$  B2 transition.  $V_0$  denotes the experimental equilibrium volumes at ambient conditions (see Table I).

data in a format suitable for Rietveld analysis using the FULLPROF program.<sup>34</sup> The lattice constants at ambient pressure have been determined as  $a_0=5.852$  and  $a_0=6.067$  Å for LaS and LaSe, respectively, in good agreement with previous experimental data given by Ref. 16.

### III. STRUCTURAL, ELASTIC, AND HIGH-PRESSURE STUDIES

#### A. Ground-state and elastic properties

The calculated ground-state properties such as equilibrium lattice constant, bulk modulus, and its pressure derivative are given in Table I. The calculated equilibrium lattice constants are generally overestimated by  $\sim 0.5\%$  compared to experiment, which is an improvement compared to earlier calculations.<sup>12,16</sup> Similarly, for the bulk modulus, the agreement between theory and experiment has improved.<sup>12,16</sup> It is interesting to note that the bulk moduli of the lanthanum chalcogenides are quite similar to those of the neighboring cerium chalcogenides, which are characterized by a localized  $f$  state:<sup>37</sup>  $B=82, 76,$  and  $58$  GPa for CeS, CeSe, and CeTe, respectively. Similarly, the calculated bulk moduli of the praseodymium chalcogenides are  $B=89, 78,$  and  $57$  GPa for PrS, PrSe, and PrTe, respectively, when Pr is represented in a trivalent configuration.<sup>38</sup> These similarities of numbers corroborate the practice of taking the lanthanum chalcogenides as nonmagnetic reference systems for the later rare-earth chalcogenides.

The calculated elastic constants of LaS, LaSe, and LaTe are listed in Table II, where we also compare to the recent linear augmented plane-wave (LAPW) calculation of Ref. 6. The two theoretical approaches find very similar  $C_{11}$  value for LaS and LaSe, while for LaTe this parameter is  $\sim 13\%$  smaller in the present calculations than found by the LAPW method. The present  $C_{12}$  and  $C_{44}$  parameters are in all cases lower than found in Ref. 6, for LaSe  $C_{12}$  with almost a factor of 2 difference. Our calculated shear moduli  $G$  are 19–40% larger than the ones calculated with LAPW. For Young's modulus  $E$ , our values are 16–35% higher and, finally, for Poisson's ratio  $\nu$ , our values are 8–17% lower than the LAPW results. The largest discrepancies between the two calculations occur for LaTe in all cases. Furthermore, we observe the general trend that the heavier the chalcogenide is, the softer the compound is. This trend is expected and easy to understand, since with increased chalcogen size, the lattice parameter increases and the valence orbitals become increasingly delocalized due to a higher number of nodes.<sup>39</sup>

As previously stated, there is at present no experimental information regarding the elastic constants available for the lanthanum chalcogenides. The elastic constants of LaS are of roughly the same magnitude as those measured for the iso-electronic YS compound (Table II).

Table III presents sound velocities and Debye temperatures, as derived from the calculated elastic constants.<sup>30</sup> The Debye temperatures have been determined experimentally from the low-temperature specific heat, and the agreement with our calculations is excellent (the calculated Debye temperatures are 0.5–6% higher than experiment), which can be taken as an indirect check on our calculated elastic constant values.

#### B. High-pressure structural transitions

The high-pressure structural behavior of the lanthanum chalcogenides was studied both experimentally and theoretically. The calculated total energies as functions of relative

TABLE III. Calculated longitudinal, shear, and average wave velocities ( $v_l$ ,  $v_s$ , and  $v_m$ , respectively) in m/s and the Debye temperature  $\theta_D$  in kelvin from the average elastic wave velocity for lanthanum monochalcogenides in the  $B1$  structure at the theoretical equilibrium volume.

Compound		$v_l$	$v_s$	$v_m$	$\theta_D$
LaS	Present	5249	3072	3406	277.2
	Expt. <sup>a</sup>				276
LaSe	Present	4626	2712	3006	233.6
	Expt. <sup>a</sup>				231
LaTe	Present	3972	2273	2524	185.7
	Expt. <sup>a</sup>				175

<sup>a</sup>Reference 3.

volume for LaS, LaSe, and LaTe are shown in Fig. 1, while experimental and theoretical pressure-volume relations are presented in Figs. 2, 4, and 5, for LaS, LaSe, and LaTe, respectively. Figure 3 shows the diffraction spectra recorded for LaS and LaSe. It appears from the theory presented in Fig. 1 that with compression, the  $B2$  phase becomes more and more favorable, and eventually a transition from the  $B1$  structure to the  $B2$  structure occurs. From the common tangent of the  $B1$  and  $B2$  total energies, the transition pressure is determined. The calculated transition pressure (Table IV) for LaS is 29.3 GPa with a volume collapse of 10.3%, which is in good agreement with the experimental transition pressure of 27–28 GPa with a volume collapse of around 9.5%, as shown in Fig. 2. A similar transition was predicted to occur in CeS around 24.3 GPa, in which the Ce ions are in a tetravalent state.<sup>41</sup> In the case of PrS, a similar transition is predicted to occur around 22 GPa, in this case with the Pr ions remaining trivalent.<sup>38</sup> The transition pressure of LaS is similar to that of the pnictogen group neighbor LaP, in which a transition from the  $B1$  structure to a distorted  $B2$  structure is observed experimentally around 24 GPa.<sup>42</sup>

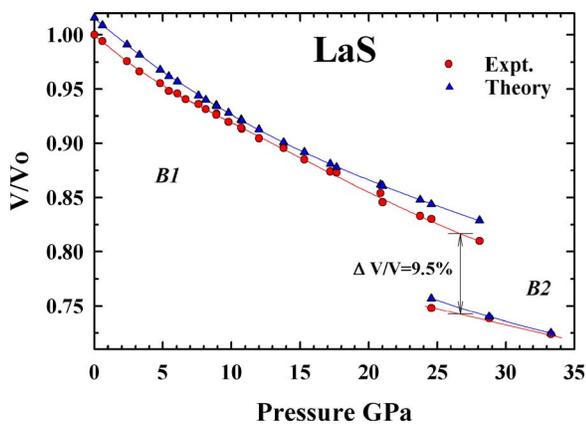
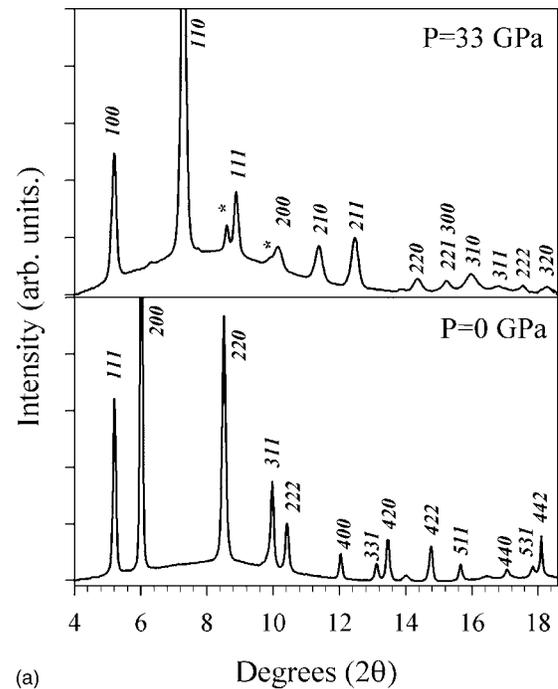
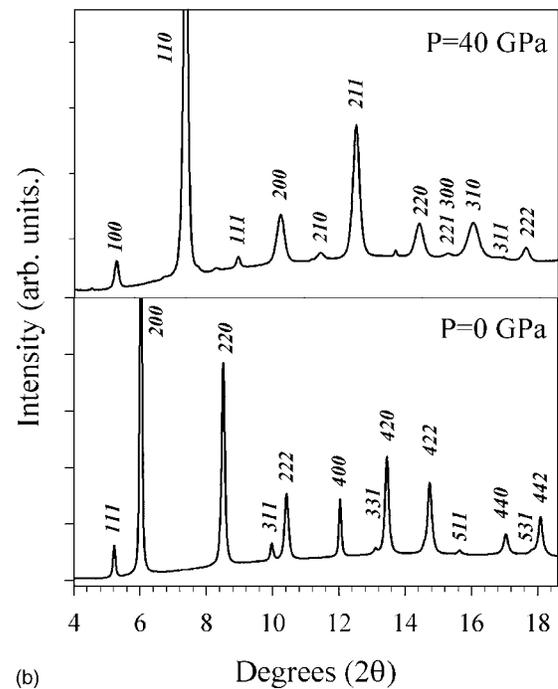


FIG. 2. (Color online) Pressure as a function of relative volume for LaS in the  $B1$  and  $B2$  structures. Triangles: theory (GGA); circles: experiment. The experimental volume collapse at the  $B1 \rightarrow B2$  transition is marked.  $V_0 = 50.10 \text{ \AA}^3$  denotes the experimental equilibrium volume at ambient conditions.



(a)



(b)

FIG. 3. X-ray-diffraction spectra of (a) LaS and (b) LaSe in the  $B1$  and  $B2$  structures. Lattice parameters at  $P=0$  GPa,  $a = 5.8520 \text{ \AA}$  and  $a = 6.0670 \text{ \AA}$  for LaS and LaSe, respectively, and in the  $B2$  structure,  $a = 3.3068 \text{ \AA}$  for LaS at  $P=33$  GPa and  $a = 3.3684 \text{ \AA}$  for LaSe at  $P=40$  GPa. Inconel gasket peaks in the LaS high-pressure phase are denoted by an asterisk. Weak extra diffraction lines in the LaSe high-pressure phase are due to the nitrogen pressure transmitting medium.

Like LaS, LaSe also undergoes a  $B1 \rightarrow B2$  transition, experimentally seen at a pressure of 19 GPa with a volume reduction of 10%, see Fig. 4, for which the present theory finds concordant values of  $P_t = 21$  GPa with a volume col-

TABLE IV. Calculated and experimental transition pressures,  $P_t$  in GPa, and volume changes, given in %, for the  $B_1 \rightarrow B_2$  structural phase transition of lanthanum monochalcogenides.

Compound	$P_t$		Volume collapse	
	Theory	Expt.	Theory	Expt.
LaS	29.3	27–28	10.3	9.5
LaSe	21	19	10.4	10.5
LaTe	9.7	7 <sup>a</sup>	10.4	

<sup>a</sup>Reference 5.

lapse of 10.4%. In the case of CeSe, a similar transition from  $B_1$  type to  $B_2$  type occurs around 20 GPa,<sup>37</sup> in this case with the Ce ion remaining trivalent on both sides of the transition according to theory.<sup>41</sup> Even for PrSe, a  $B_1 \rightarrow B_2$  transition is predicted to occur around 12 GPa, wherein the Pr ions remain trivalent.<sup>38</sup> The transition pressure of LaSe is similar to that of the pnictogen neighbor LaAs, in which a transition from  $B_1$  structure to a distorted  $B_2$  type occurs around 20 GPa.<sup>43</sup>

As far as LaTe is concerned, a transition from  $B_1$  type to  $B_2$  type is reported around 7 GPa,<sup>5</sup> which agrees quite well with the calculated transition pressure of 9.7 GPa with a volume reduction of 10.4%, see Fig. 5. Both CeTe and PrTe undergo a transition from  $B_1$  type to  $B_2$  type around  $8 \pm 1$  (Ref. 44) and  $9 \pm 1$  GPa.<sup>45</sup> When comparing the pnictogen neighbor LaSb with that of LaTe, the pnictogen undergoes a transition from  $B_1$ -type to a distorted  $B_2$ -type structure around 11 GPa,<sup>46</sup> which is slightly higher than that of LaTe.

#### IV. CONCLUSIONS

By means of a combined theoretical and experimental study, the high-pressure structural behavior of LaX ( $X = S, Se, Te$ ) compounds have been investigated. Unlike the lanthanum monpnictides which show a transition from  $B_1$

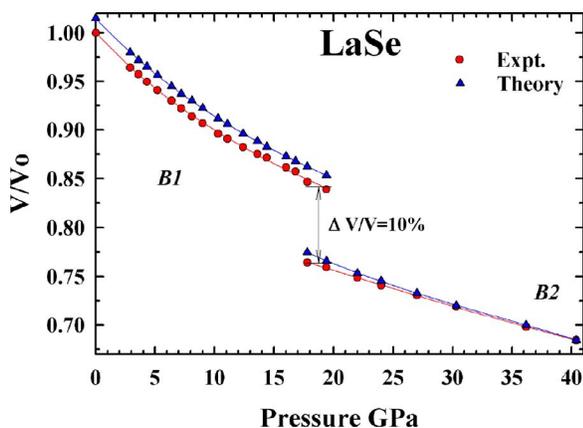


FIG. 4. (Color online) Pressure as a function of relative volume for LaSe in the  $B_1$  and  $B_2$  structures. Triangles: theory (GGA); circles: experiment. The experimental volume collapse at the  $B_1 \rightarrow B_2$  transition is marked.  $V_0 = 55.83 \text{ \AA}^3$  denotes the experimental equilibrium volume at ambient conditions.

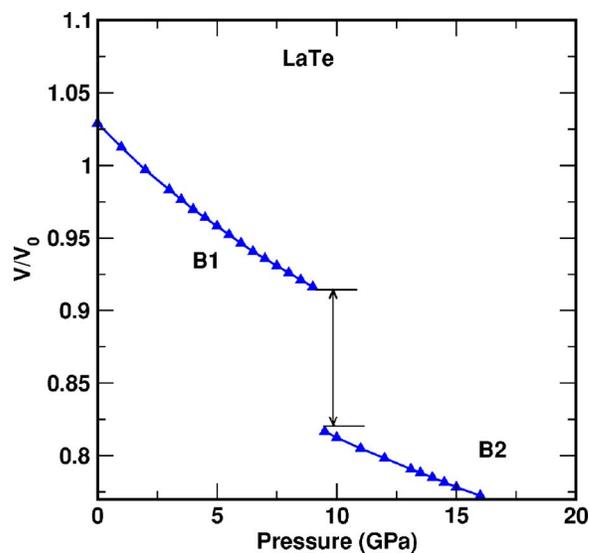


FIG. 5. (Color online) Theoretical pressure as a function of relative volume for LaTe in the  $B_1$  and  $B_2$  structures.  $V_0 = 66.62 \text{ \AA}^3$  denotes the experimental equilibrium volume at ambient conditions (Ref. 10).

to a distorted  $B_2$  structure,<sup>47,48</sup> the lanthanum monochalcogenides exhibit a simple  $B_1 \rightarrow B_2$  structural phase transition similar to the one found for most of the lanthanide and actinide monochalcogenides studied up to now.<sup>2,49–53</sup> The trend in the high-pressure behavior of the lanthanum chalcogenides fits into the general picture of the rare-earth and actinide chalcogenides.<sup>2</sup> The bulk modulus as well as the transition pressure for the structural  $B_1 \rightarrow B_2$  transition decreases from LaS to LaSe and further on to LaTe, i.e., as the ligand ionic radius increases, while the volume at the transition point slightly increases ( $V/V_0 \approx 0.82, 0.84,$  and  $0.88$  on the  $B_1$  side for LaS, LaSe, and LaTe, respectively).

For all three systems studied here, the volume collapse is around 10% (from both experiment and theory) at the  $B_1 \rightarrow B_2$  transition. Let us compare this magnitude of the volume collapse to a very simple model in which we assume that at the transition point, the La–X bond length is restored to the ambient value. We expect such a model to underestimate the volume collapse, since the bond length at high pressure will most probably be a bit smaller than at ambient pressure. Our simple model gives the following relation between the relative volume  $V_t^{B_1}/V_0^{B_1}$  just before the transition and the volume collapse  $1 - V_t^{B_2}/V_t^{B_1}$ ,

$$1 - \frac{V_t^{B_2}}{V_t^{B_1}} = 1 - \frac{4}{3\sqrt{3}} \frac{V_0^{B_1}}{V_t^{B_1}}. \quad (1)$$

For LaS, the experimental relative volume at the transition is 0.82, which would give a volume collapse of 6% according to this model. For LaSe, the corresponding numbers are 0.84 and 8%. Thus, the volume collapse observed experimentally (and from density-functional calculations) can be viewed as a partial restoration of the original bond length between the La and the chalcogenide. Based on the above discussion, we conclude that the volume collapse observed in the lanthanum chalcogenides is entirely consistent with a simple picture of

the transition in which the volume collapse is a consequence of the rearrangement of the atoms to a more close-packed structure while the total number of valence electrons remains unchanged. We have also checked the partial occupation number of *spdf* states across the structural transition and there is no appreciable change in the occupation numbers across the transition. This is in contrast to the situation in many Ce systems, in which the volume collapse is accompanied by delocalization of an *f* electron.<sup>41,54–56</sup>

## ACKNOWLEDGMENTS

G.V., V.K., A.D., and B.J. acknowledge V. R. and SSF for financial support and SNIC for computer time. The authors (S.H., M.I., and T.L.B.) would like to thank K. Mattenberger and O. Vogt (ETH, Zürich) for the samples used in this study. Support given to M.I. within the framework of the EC funded program “Human capital and mobility” is also acknowledged.

\*Corresponding author. Electronic address: [vaithee@kth.se](mailto:vaithee@kth.se)

- <sup>1</sup>A. Jayaraman, P. D. Dernier, and L. D. Longinotti, *High Temp. - High Press.* **7**, 1 (1975).
- <sup>2</sup>U. Benedict, *J. Alloys Compd.* **223**, 216 (1995).
- <sup>3</sup>E. Bucher, K. Andres, F. J. di Salvo, J. P. Maita, A. C. Gossard, A. S. Cooper, and G. W. Hull, Jr., *Phys. Rev. B* **11**, 500 (1975).
- <sup>4</sup>T. Le Bihan, A. Bombardi, M. Idiri, S. Heathman, and A. Lindbaum, *J. Phys.: Condens. Matter* **14**, 10595 (2002).
- <sup>5</sup>A. Jayaraman, *Bull. Am. Phys. Soc.* **24** (3), 397 (1979).
- <sup>6</sup>A. Bouhemadou, R. Khenata, and M. Maamache, *J. Mol. Struct.: THEOCHEM* **777**, 5 (2006).
- <sup>7</sup>M. Nakayama, T. Ito, H. Kumigashira, H. Matsui, H. Komatsu, T. Takahashi, H. Aoki, and A. Ochiai, *J. Magn. Magn. Mater.* **272-276**, e121 (2004).
- <sup>8</sup>M. Nakayama, H. Aoki, A. Ochiai, T. Ito, H. Kumigashira, T. Takahashi, and H. Harima, *Phys. Rev. B* **69**, 155116 (2004).
- <sup>9</sup>M. Nakayama, N. Kimura, H. Aoki, C. Terakura, T. Terashima, S. Uji, and A. Ochiai, *J. Magn. Magn. Mater.* **272-276**, e93 (2004).
- <sup>10</sup>M. Nakayama, N. Kimura, H. Aoki, A. Ochiai, C. Terakura, T. Terashima, and S. Uji, *Phys. Rev. B* **70**, 054421 (2004).
- <sup>11</sup>S. V. Vlasov and O. V. Farberovich, *Solid State Commun.* **56**, 967 (1985).
- <sup>12</sup>Z. W. Lu, D. J. Singh, and H. Krakauer, *Phys. Rev. B* **37**, 10045 (1988).
- <sup>13</sup>S. Sankaralingam, S. M. Jaya, G. Pari, and R. Asokamani, *Phys. Status Solidi B* **174**, 435 (1992).
- <sup>14</sup>O. Eriksson, J. Wills, P. Mumford, M. Cahay, and W. Friz, *Phys. Rev. B* **57**, 4067 (1998).
- <sup>15</sup>O. Eriksson, M. Cahay, and J. M. Wills, *Phys. Rev. B* **65**, 033304 (2001).
- <sup>16</sup>G. Vaitheeswaran, V. Kanchana, and M. Rajagopalan, *J. Phys. Chem. Solids* **64**, 15 (2003).
- <sup>17</sup>V. N. Antonov, B. N. Harmon, and A. N. Yaresko, *Phys. Rev. B* **69**, 094404 (2004).
- <sup>18</sup>R. R. Yadav and D. Singh, *J. Phys. Soc. Jpn.* **70**, 1825 (2001).
- <sup>19</sup>D. Varshney, N. Kaurav, P. Sharma, S. Shah, and R. K. Singh, *Phys. Status Solidi B* **241**, 3179 (2004).
- <sup>20</sup>D. Varshney, N. Kaurav, R. Kinge, S. Shah, and R. K. Singh, *High Press. Res.* **25**, 145 (2005).
- <sup>21</sup>I. Frankowski and P. Wachter, *Solid State Commun.* **40**, 885 (1985).
- <sup>22</sup>W. Beckenbaugh, J. Evers, G. Güntherodt, E. Kaldis, and P. Wachter, *J. Phys. Chem. Solids* **36**, 239 (1975).
- <sup>23</sup>M. M. Steiner, H. Eschrig, and R. Monnier, *Phys. Rev. B* **45**, 7183 (1992).
- <sup>24</sup>R. Pittini, J. Schoenes, F. Hulliger, and P. Wachter, *Phys. Rev. Lett.* **78**, 725 (1997).
- <sup>25</sup>R. Pittini and P. Wachter, *J. Magn. Magn. Mater.* **177-181**, 1025 (1998).
- <sup>26</sup>F. Salghetti-Drioli, P. Wachter, and L. Degiorgi, *Solid State Commun.* **109**, 773 (1999).
- <sup>27</sup>S. Y. Savrasov, *Phys. Rev. B* **54**, 16470 (1996).
- <sup>28</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- <sup>29</sup>F. Birch, *J. Appl. Phys.* **9**, 279 (1938).
- <sup>30</sup>V. Kanchana, G. Vaitheeswaran, A. Svane, and A. Delin, *J. Phys.: Condens. Matter* **18**, 9615 (2006).
- <sup>31</sup>H. K. Mao, J. Xu, and P. M. Bell, *J. Geophys. Res.* **91**, 4673 (1986).
- <sup>32</sup>M. Thoms, S. Bauchau, D. Häusermann, M. Kuntz, T. Le Bihan, M. Mezouar, and D. Strawbridge, *Nucl. Instrum. Methods Phys. Res. A* **413**, 175 (1998).
- <sup>33</sup>A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch, and D. Häusermann, *High Press. Res.* **14**, 235 (1996).
- <sup>34</sup>J. Rodriguez-Carvajal, *Physica B* **192**, 55 (1993).
- <sup>35</sup>S. Von Molnar, T. Penny, and F. Holtzberg, *J. Phys. (Paris)* **37**, C4-241 (1976).
- <sup>36</sup>A. Jayaraman, B. Batlogg, R. G. Maines, and H. Bach, *Phys. Rev. B* **26**, 3347 (1982).
- <sup>37</sup>J. M. Léger, *Physica B* **190**, 84 (1993).
- <sup>38</sup>G. Vaitheeswaran, L. Petit, A. Svane, V. Kanchana, and M. Rajagopalan, *J. Phys.: Condens. Matter* **16**, 4429 (2004).
- <sup>39</sup>A. Delin, P. Ravindran, O. Eriksson, and J. M. Wills, *Int. J. Quantum Chem.* **69**, 349 (1998); A. Delin and T. Klüner, *Phys. Rev. B* **66**, 035117 (2002).
- <sup>40</sup>P. D. Dernier, W. Weber, and L. D. Longinotti, *Phys. Rev. B* **14**, 3635 (1976).
- <sup>41</sup>A. Svane, W. Temmerman, and Z. Szotek, *Phys. Rev. B* **59**, 7888 (1999).
- <sup>42</sup>T. Adachi, I. Shirovani, J. Hayashi, and O. Shimomura, *Phys. Lett. A* **250**, 389 (1998).
- <sup>43</sup>I. Shirovani, K. Yamanashi, J. Hayashi, N. Ishimatsu, O. Shimomura, and T. Kikegawa, *Solid State Commun.* **127**, 573 (2003).
- <sup>44</sup>J. M. Léger, R. Epain, J. Loriers, D. Ravot, and J. Rossat-Mignod, *Phys. Rev. B* **28**, 7125 (1983).
- <sup>45</sup>A. Chatterjee, A. K. Singh, and A. Jayaraman, *Phys. Rev. B* **6**, 2285 (1972).
- <sup>46</sup>J. Hayashi, I. Shirovani, Y. Tanaka, T. Adachi, O. Shimomura, and T. Kikegawa, *Solid State Commun.* **114**, 561 (2000).
- <sup>47</sup>G. Vaitheeswaran, V. Kanchana, and M. Rajagopalan, *J. Alloys Compd.* **336**, 46 (2002).
- <sup>48</sup>G. Vaitheeswaran, V. Kanchana, and M. Rajagopalan, *Physica B*

- 315**, 64 (2002).
- <sup>49</sup>S. Dabos-Seignon, U. Benedict, S. Heathman, J. C. Spirlet, and M. Pages, *J. Less-Common Met.* **160**, 35 (1990).
- <sup>50</sup>M. Gensini, E. Gering, S. Heathman, U. Benedict, and J. C. Spirlet, *High Press. Res.* **2**, 347 (1990).
- <sup>51</sup>L. Gerward, J. S. Olsen, U. Benedict, S. Dabos, and O. Vogt, *High Press. Res.* **1**, 235 (1989).
- <sup>52</sup>T. Le Bihan, S. Darracq, S. Heathman, U. Benedict, K. Mattenberger, and O. Vogt, *J. Alloys Compd.* **226**, 143 (1995).
- <sup>53</sup>T. Le Bihan, S. Heathman, and J. Rebizant, *High Press. Res.* **15**, 387 (1997).
- <sup>54</sup>B. Johansson, *Philos. Mag.* **30**, 469 (1974).
- <sup>55</sup>A. Delin, P. M. Oppeneer, M. S. S. Brooks, T. Kraft, J. M. Wills, B. Johansson, and O. Eriksson, *Phys. Rev. B* **55**, R10173 (1997).
- <sup>56</sup>A. Svane, Z. Szotek, W. M. Temmerman, and H. Winter, *Solid State Commun.* **102**, 473 (1997).