Thermal properties of CaMoO_4 : Lattice dynamics and synchrotron powder diffraction studies

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(Received 6 October 2005; revised manuscript received 7 November 2005; published 11 January 2006)

The structure of calcium molybdate was studied by means of synchrotron based high-resolution powder diffraction methods in the temperature range 12–300 K. The scheelite structure type was confirmed for CaMoO_4 in the temperature region investigated and no structural anomalies were observed. Thermal expansion coefficients extracted from the thermal dependencies of the cell sizes are found to be in good agreement with the predictions from our lattice dynamics calculations that form the background for microscopic interpretation of the experimental data. From the analyses of experimental results and the calculated thermal expansion coefficients, elastic constants, phonon density of states, heat capacities, entropy, and Grüneisen parameters it is concluded that a quasiharmonic lattice dynamics approach provides a good description of these properties for CaMoO_4 at temperatures below 800 K.

DOI: [10.1103/PhysRevB.73.014104](https://doi.org/10.1103/PhysRevB.73.014104)

PACS number(s): 65.40.-b, 63.20.Dj, 61.10.Nz, 62.20.Dc

I. INTRODUCTION

Materials belonging to the tungstate and molybdate families have for decades been the object of extensive studies. The interest has been driven by the fact that these compounds have excellent optical properties, making them especially suitable for a number of applications such as phosphors,¹ laser hosts,² and scintillators.³ In such applications the luminescence properties of these compounds are of particular importance; this resulted in a huge legacy of research work, some of which is described in Refs. 4–8.

A new field for the application of these materials has emerged a few years ago when a new generation of cryogenic detectors, offering the capability of discrimination between electron and nuclear recoils has been implemented in some particle physics experiments. Different types of interactions (electron and nuclear recoils) can be identified by simultaneously measuring a combination of phonon and scintillation signals from cryogenic phonon-scintillation detectors (CPSD), operating at temperatures in the milli-kelvin range.⁹ This technique provides unrivalled sensitivity and the unique advantage of background identification and discrimination that is crucially important for rare-event and low-background physics experiments. Therefore, CPSDs play an important role in experiments searching for rare events, so as interactions with weakly interacting massive particles (WIMP), possibly constituting the galactic dark matter.^{10,11} A clear demonstration of this technique's effectiveness derives from a recent upper limit for the scalar cross section of WIMP-nucleon elastic scattering, obtained in a search for dark matter.¹²

A further advantage of the CPSD technique is the possibility of using different target materials, which allows ex-

ploiting the material signature for the confirmation of a WIMP signal.¹³ The only material used so far is CaWO_4 but research and development is underway for the implementation of additional new scintillation targets into cryogenic dark matter searches.¹⁴ Recently, ZnWO_4 has been identified as an attractive target material¹⁵ and our research has now widened to include molybdate crystals. Of particular importance is calcium molybdate that is isostructural with CaWO_4 and exhibits sufficient light yield.¹⁶ Given that the expected ratio of WIMP-nucleon interactions in these two crystals varies appreciably with energy, it is argued that CaMoO_4 can be an excellent complementary material to calcium tungstate in a multitarget cryogenic search for dark matter. Therefore the luminescence and scintillation properties of CaMoO_4 are currently the subject of our intensive studies.^{16–18}

Although a high light yield at low temperatures is a key selection criterion for a material for CPSD application but in addition a number of other properties, such as surface stability, thermodynamic properties of the lattice, crystal structure, and phonon propagation properties that can be of similar importance. Especially the use of a material as CPSD relies on the efficiency of phonon transport through the crystal and as a consequence of this knowledge of lattice dynamics (LD) is of great relevance. So far there is a lack of information on the above properties not only for the prospective materials, but even for well-known scintillation materials when low-temperature applications are considered.

To address this problem we turned our attention to modeling techniques and recently it was demonstrated that quasiharmonic lattice dynamics and the static lattice minimization method are viable tools for the characterization of LD of calcium tungstate.¹⁹ The success of this approach stimulated

our interest in the modeling of LD of other materials of interest and in this paper we present the results of such studies carried out for CaMoO_4 . The objective of this work is thus to verify the validity of the model for another material and to establish thermodynamic characteristics of the crystals that are relevant in the planned use of calcium molybdate for the CPSD technique.

II. X-RAY DIFFRACTION (XRD) EXPERIMENT

We used calcium molybdate crystals grown by the Czochralski technique. A preliminary phase analysis was performed by powder x-ray diffraction on a Siemens D500 diffractometer using Cu radiation and a secondary monochromator (2θ 5° – 110°). Structural properties as a function of temperature were studied using the high-resolution powder diffraction technique with synchrotron radiation. The experiments were carried out at the beamline B2 (Ref. 20) of HASYLAB on a high-resolution powder diffractometer equipped with a closed-cycle helium cryostat. All measurements were performed in Debye-Scherrer geometry (0.3 mm capillaries) using the Image Plate detector OBI.²¹ To reduce absorption and fluorescence an x-ray wavelength of 0.4996 Å was chosen.

The measurements were carried out in the temperature range 12–300 K. First, the sample was cooled from room temperature to 12 K and 37 diffraction patterns in the 2θ region 2° – 40° were collected during cooling. The temperature was then stabilized at 12 K and another set of powder diffraction patterns was collected in the temperature range 20–300 K with temperature increments of 20 K. The measured XRD data were analyzed using the full profile Rietveld method implemented in the WinCSD program package.²²

III. COMPUTATIONAL METHODOLOGY

A major effort has been made to construct a model of interatomic interaction that allows a proper description of the LD for the crystal of interest. To do this we carried out a number of quasiharmonic lattice dynamics simulations using the methodology that is described in detail elsewhere.²³ The simulations performed in this study use a modification of the Born model of solids that consider a material as a collection of point charges with electrostatic and short-range interactions. The summation of electrostatic interactions was performed in real and reciprocal space according to the Ewald method to ensure proper convergence. The electrostatic potential is given by the well-known Coulomb formula

$$U_{ij}^{\text{Coul}}(r_{ij}) = \frac{Z_i Z_j e^2}{r_{ij}}, \quad (1)$$

where e is the charge of an electron and Z_i and Z_j are the effective charges of the i th and j th atoms, respectively. The atomic charge of calcium Z_{Ca} was chosen to be equal to its chemical valence. For a modeling of the covalent Mo-O bonds caused by hybridization between the d orbitals of Mo and $2p$ orbitals of O atomic charge of molybdenum Z_{Mo} was allowed to vary during fitting. The electroneutrality condition was met by the constraint $Z_{\text{O}} = -\frac{1}{4}(Z_{\text{Ca}} + Z_{\text{Mo}})$.

In the modeling of atomic interactions we used the linear combination of Coulomb and repulsion potentials. The repulsion potential for Ca-O and O-O interactions is presented as a sum of Born-Mayer and van der Waals energies (the so-called Buckingham potential), which is usually used for simulations of ionic compounds and bonds

$$U_{ij}^{\text{Buck}}(r_{ij}) = b_{ij} \exp\left\{\frac{\rho_{ij}}{r_{ij}}\right\} - \frac{c_{ij}}{r_{ij}^6} \quad (2)$$

with b_{ij} , c_{ij} , and ρ_{ij} being the Buckingham potential parameters. For the modeling of partially covalent Mo-O bonds the analytical form of the Morse potential is preferable

$$U_{ij}^{\text{Morse}}(r_{ij}) = D([1 - \exp\{-a_m(r_{ij} - r_0)\}]^2 - 1). \quad (3)$$

Here D , a_m , and r_0 are the Morse potential parameters. Additional interactions within complex anions were simulated using a three-body O-Mo-O potential. In the present study the analytical form proposed by Sanders *et al.*²⁴ was chosen:

$$U_{ijk}^{\text{Three}}(\theta_{ijk}) = \frac{1}{2}k_{\text{Three}}[\theta_{ijk} - \theta_0^2], \quad (4)$$

where θ_{ijk} is the angle between i th, j th, and k th atoms and k_{Three} is a force constant. The value of the angle in the three-body interaction was selected as 1.9337 rad ($110^\circ 51'$), based on the analysis of the available structural data.²⁵

In our simulation we neglected the short-range contribution to the cation-cation interactions since the cations tend to be contracted, which leads to a negligible overlap of the electron density and a low polarizability. The latter results in only a small contribution from the van der Waals attraction. Because of the low polarizability of the cations, we also neglected the dispersion term for the cation-anion interactions. The errors associated with these approximations are merged into the errors of the resultant parameters. The major qualitative improvement of our model for calcium molybdate over the previously reported one for CaWO_4 (Ref. 19) is in recognizing the fact that different potentials are needed to describe the interaction *between* and *within* the molecular anion MoO_4^{2-} . Therefore for intramolecular O-O interaction we used the Buckingham potential in the form derived by Gavezotti,²⁶ whereas the parameters of the intermolecular O-O Buckingham potential were defined in the course of the simulations.

Room temperature structural data²⁵ and seven independent elastic constants²⁷ reported for CaMoO_4 were fitted simultaneously by means of the free energy minimization and the “relax” fitting technique²⁸ using the GULP (general utility lattice program) code.^{29,30} It should be noted that the determination of elastic constants in Ref. 31 (used by Farley and Saunders²⁷) is based on ultrasonic velocity measurements that give adiabatic values, while the free energy minimization technique derives characteristic quantities for isothermal process. However, as was shown by Gluyas *et al.*,³² for calcium tungstate the discrepancy between adiabatic and

TABLE I. Experimental and calculated properties of CaMoO₄ at $T=300$ K and $P=1$ atm.

Structural parameters		
Properties	Experiment ^a	Calculations ^b
a (Å)	5.222(1)	5.230729
c (Å)	11.425(3)	11.433496
Ca, $4b$ $x/a, y/a, z/c$	0, 0, $\frac{1}{2}$	0, 0, $\frac{1}{2}$
Mo, $4a$ $x/a, y/a, z/c$	0, 0, 0	0, 0, 0
O, $16f$ x/a	0.2436(6)	0.245550
y/a	0.1490(6)	0.147445
z/c	0.0842(3)	0.084430
Elastic constants		
Properties	Experiment ^c	Calculations ^b
c_{11} , GPa	144	144.5
c_{33} , GPa	126	125.8
c_{44} , GPa	36.9	34.5
c_{66} , GPa	46.1	49.4
c_{12} , GPa	64.8	62.6
c_{13} , GPa	44.8	43.3
c_{16} , GPa	-14.2	-13.8

^aReference 25.^bOur data.^cReference 27.

isothermal elastic constants is less than 1% at room temperature. Therefore, the use of experimental values for the elastic constants in our simulation is justified.

The present studies are performed without the zero static internal stress approximation and both internal and strain variables are optimized with respect to the free energy. The cut-off for Ca-O and intermolecular O-O Buckingham potentials was chosen at 12 Å, whereas intramolecular interactions were limited by the respective Mo-O bond lengths (Ref. 33). As a first approximation in the calculation of CaMoO₄ we applied the parameters of Ca-O, W-O, and O-W-O interactions derived for CaWO₄.¹⁹ The results of experimental measurements and theoretical modeling are collated in Table I, while Table II lists the values of the interaction parameters that give the best fit. It should be noted that the deviations obtained between calculated and experimental lattice parameters (less than 1%) and elastic constants (less than 7%) are very reassuring for semiclassical calculations. Clearly, it is smaller than for calcium tungstate that indicates the improvement in the prediction abilities of the model.

IV. RESULTS AND DISCUSSION

A. Structure and thermal expansion

The room temperature structure of calcium molybdate has been studied for a long time by different authors.^{25,34–36} At room temperature, CaMoO₄ belongs to the scheelite type of structure (space group $I4_1/a$, No 88 in the International Tables of Crystallography), exhibiting a complex layer struc-

TABLE II. Parameters of interactions for CaMoO₄.

Coulomb potential Eq. (1)			
Atoms	Z_i, e		
Ca	2.0000		
W	1.7083		
O	−0.9271		
Buckingham potential Eq. (2)			
Atomic pairs	b (eV)	ρ (Å)	c (eV Å ⁶)
Ca-O	2824.5	0.2724	0.00
O-O (intra)	2023.8	0.2674	13.83
O-O (inter)	8502.0	0.2260	0.00
Morse potential Eq. (3)			
Atomic pairs	D (eV)	a_m (Å ^{−2})	r_0 (Å)
Mo-O (intra)	2.1674	2.9093	1.7805
Three-body potential Eq. (4)			
Three-bodies	k_{Three} (eV rad ^{−2})		θ_0 (rad)
O-Mo-O (intra)	5.1563		1.9337

ture with the layers perpendicular to the c axis. Each layer has a two-dimensional CsCl type arrangement of a Ca cation and complex anion MoO₄⁻², which are surrounded by eight ions of the opposite sign. A fragment of the crystal structure is shown in Fig. 1.

The x-ray diffraction pattern obtained from preliminary analysis shows no presence of additional phases. From the results of pulsed electron paramagnetic resonance and dielec-

FIG. 1. (Color online) Crystal structure of CaMoO₄.

tric studies carried out by Simon *et al.*³⁷ it was concluded that CaMoO_4 undergoes a second-order ferroelastic phase transition at $T_c=52$ K analogous to that observed in the isostructural scheelite compounds BiVO_4 and LaNaO_4 . However, we did not observe visible structural changes in CaMoO_4 at temperatures below 52 K. Neither a splitting nor systematic broadening of the specific reflections were noticed in the diffraction patterns collected at 12, 20, and 40 K within the given instrumental resolution (typical full width at half maximum values were 0.055° – 0.07°). Full profile Rietveld refinement of the CaMoO_4 structure at 12 K, performed in the monoclinic structure model (proposed for LaNbO_4 in Ref. 38) did not lead to the improvement of the residuals comparing with the tetragonal one. The obtained values of the lattice parameters of the monoclinic cell in space group $I2/c$ [$a=5.2175(9)$ Å, $b=11.3969(5)$ Å, $c=5.2164(9)$ Å, $\beta=89.98(2)^\circ$] do not deviate from the tetragonal ones [$a=5.2169(2)$ Å, $c=11.3962(5)$ Å] within the limit of uncertainty. Furthermore, no deviations from the atomic positions were noticed for the Ca and Mo atoms. Finally, it should be noted that Raman spectroscopy studies that are especially sensitive to the ferroelectric phase transitions revealed no phase transformation in CaMoO_4 at low-temperature and ambient pressure (see Ref. 39) being consistent with the result of present study.

Because of this the crystal structure of CaMoO_4 was considered to be scheelite over the temperature range 12–800 K. There is appreciable anisotropy of thermal expansion in CaMoO_4 : the thermal expansion in the $[100]$ direction is of about 55% of that in the $[001]$ direction of the tetragonal cell. The lattice parameters increase with temperature in a nonlinear fashion (see Fig. 2). Thermal dependences of the lattice parameters obtained during cooling (open squares) and at fixed temperature during heating (solid squares) coincide within the experimental error, indicating good response of the sample to temperature changes. Lattice parameters obtained during cooling were presented only for comparison and were excluded from further considerations. Figure 2 shows that the low-temperature part of the $l(T)$ dependence measured by us can be linked up fairly well with the high-temperature one obtained by Deshpande and Suryanarayana.⁴⁰

For uniaxial crystals the thermal expansion tensor α_{kl} has two independent components $\alpha_a=\alpha_{11}$ and $\alpha_c=\alpha_{33}$, where α_a and α_c denote the thermal expansion coefficient (TEC) in the a and c directions, respectively. The volumetric TEC α_v can be obtained by summation of the respective anisotropic TECs: $2\alpha_a+\alpha_c$. Cell sizes (lattice parameters and cell volume) $l(T)$ are related to the TEC $\alpha_l(T)$ through the V - T equation of state as

$$l(T) = l(T_0) \exp \left\{ \int_{T_0}^T \alpha_l(x) dx \right\}, \quad (5)$$

where T_0 stands for the initial temperature; 12 K in the present studies. Usually thermal behavior of the expansion coefficient exhibits a complex shape which is poorly described by polynomial functions. Liarokapis *et al.*⁴¹ proposed the following empirical expression for TEC

FIG. 2. (Color online) Thermal dependencies of lattice parameters and the cell volume of CaMoO_4 . Squares, results of our experimental studies; circles, data from Ref. 40. Dashed curves show results of the fit to Eqs. (5) and (6), the solid line shows thermal dependence of the cell volume reconstructed via Eq. (5) from calculated thermal expansion coefficient (*vide infra*).

$$\alpha_l(T) = \left(\frac{a_0}{T} + \frac{a_1}{T^2} \right) \sinh^{-2} \left(\frac{a_2}{T} \right), \quad (6)$$

which fits $\alpha_l(T)$ better and has been used successfully in an estimation of $\alpha_v(T)$ for CaMoO_4 .³⁹ The lattice parameters obtained were fitted by Eqs. (5) and (6) and the results of the fit are presented in Fig. 2 by the dashed curves. The numerical parameters of the fit [$l(T_0)$, a_0 , a_1 and a_2] are summarized in Table III.

Using the above model of interatomic interactions and the free energy minimization technique we carried out simulations of structural properties of CaMoO_4 . The calculated thermal changes of the cell volume calculated from volumetric TEC α_v are shown in Fig. 2 as a solid line together with the experimental data.

TABLE III. The results of the lattice parameters fit to Eqs. (5) and (6).

	Lattice parameter a (Å)	Lattice parameter c (Å)
$l(T_0)$	5.2177 ± 0.0005	11.397 ± 0.001
$a_0 \times 10^{-5}$	2.63 ± 1.22	-2.42 ± 1.81
a_1	0.17 ± 0.05	0.38 ± 0.05
a_2	138 ± 13	145 ± 6
$1 - \chi^2$	4.04×10^{-5}	6.53×10^{-5}

The volumetric TEC can be expressed via fundamental parameters of solids, such as the Grüneisen parameter γ , bulk modulus K , molar volume V_m , heat capacity C , phonon frequencies ω , and the internal energy U

$$\alpha_V = \frac{1}{KV_m} \left[C\gamma + \left(\frac{\partial \omega}{\partial T} \right)_V U \right]. \quad (7)$$

At low temperatures the crystal behaves like a harmonic solid and the dependence of the phonon frequencies on temperature is negligibly small allowing one to ignore the second term of Eq. (7). This is an underlying principle of the quasiharmonic approximation and applying it accordingly, Eq. (8) translates as

$$\alpha_V = \frac{\gamma_V \rho C_V}{K_T} = \frac{\gamma_V \rho C_P}{K_S}, \quad (8)$$

where γ_V is the Grüneisen parameter, ρ is the density of the material, K_T and K_S are isothermal and adiabatic bulk modules, and C_V or C_P are the heat capacities at constant volume and pressure, respectively.

As was shown in Ref. 19, a calculation of LD within the quasiharmonic approximation for calcium tungstate becomes unreliable for temperatures above 800 K. A similar feature was also observed in the present studies and therefore we limited our considerations to temperatures $T \leq 800$ K. To get insight into the origin of thermal expansion we proceed to a detailed discussion of the individual terms in Eq. (8).

B. Density and elastic modules

The density of CaMoO₄ was calculated from the cell volume and known stoichiometry on the assumption of a perfect crystal. Thermal expansion is also dependent of the bulk modulus, either isothermal or adiabatic, which can be calculated from the known tensor of elastic constants. In the 1970s, there has been discussion on the values of the elastic constants of CaMoO₄ determined by Alton and Barlow³¹ and Wachtman *et al.*⁴² from measurements of the velocities of ultrasonic waves. Farley and Saunders,²⁷ Chung *et al.*,⁴³ and James⁴⁴ recalculated the elastic constants of calcium molybdate from the velocity measurements of Alton and Barlow. Taking the results of all these investigations as inputs we determined bulk (K) and shear (G) moduli using the formulas of Reuss and Voigt:

$$\begin{aligned} K^{\text{Voigt}} &= (2c_{11} + c_{33} + 2c_{12} + 4c_{13})/9, \\ G^{\text{Voigt}} &= (2c_{11} + c_{33} - c_{12} - 2c_{13} + 6c_{44} + 3c_{66})/9, \\ K^{\text{Reuss}} &= (2s_{11} + s_{33} + 2s_{12} + 4s_{13})^{-1}, \\ K^{\text{Reuss}} &= [(8s_{11} + 4s_{33} - 4s_{12} - 8s_{13} + 6s_{44} + 3s_{66})/15]^{-1}, \end{aligned} \quad (9)$$

where c_{ij} and s_{ij} represent the elastic constants and elastic compliances in Voigt notation. The adiabatic bulk and shear moduli were then averaged following the Hill approach and values of $K=80.5 \pm 0.5$ GPa and $G=40.9 \pm 0.3$ GPa were ob-

FIG. 3. (Color online) Calculated elastic moduli of CaMoO₄.

tained. The isothermal bulk moduli at room temperature reported in Refs. 25 and 45 are equal to 81.5(7) GPa and 82.5(7) GPa, respectively.

Finally the elastic constant matrix of CaMoO₄ was calculated from second derivatives of the energy density with respect to external strain. Thermal dependencies of bulk and shear moduli calculated from the elastic constant tensor via the Voigt-Reuss-Hill scheme are presented in Fig. 3 as solid points.

C. Phonon and thermodynamic properties

The next property to consider is the lattice heat capacity, which gives the most prominent contribution to thermal expansion. In order to do this the phonon density of states (PDOS) should be analyzed first. Anderson⁴⁶ formulated the following proviso to derive a reasonable $C_V(T)$ from PDOS: there should be no gaps in the phonon spectrum; not many modes should have frequencies above the maximum Debye frequency; the phonon density of states should be close to a parabolic law of phonon dispersion, at least in the low-energy limit.

The phonon spectrum was calculated using Born-von Karman equations of lattice dynamics. Phonon frequencies were derived for a grid of $(12 \times 12 \times 12)$ points. The PDOS was obtained by numerical integration across the Brillouin zone at each point of the grid, multiplied by the appropriate weight, being the inverse number of the quantity of grid points for a simple regular grid.⁴⁷

Clearly, as is seen in Fig. 4(a), none of the Anderson criteria is satisfied completely for the obtained PDOS of CaMoO₄. Therefore, the calculations of the thermodynamic properties, in particular, of the specific heat capacity, are not reliable within the framework of the classical Debye model. Moreover, the contribution of the individual constituents to the total PDOS does not exhibit an “acoustic character.” That is when all atoms at each frequency give a constant contribution to the total DOS, determined by relative masses and the number of atoms of each sort. An analysis of the contributions of the calcium, molybdenum, and oxygen atoms to the total PDOS shows that molybdenum dominates in the low-frequency lattice modes and in the internal modes of

FIG. 4. (Color online) (a) The phonon density of states of CaMoO_4 and contributions of constituents at 300 K and 1 atm; (b) The contribution of phonons of energy E to the volume thermal expansion as a function of E at 12 K (curve 1), 50 K (curve 2), 100 K (curve 3), 300 K (curve 4), and 800 K (curve 5).

MoO_4^{-2} tetrahedral, calcium gives a noticeable contribution at the intermediate frequency region of the phonon spectrum. Accordingly, oxygen atoms give rise to both lattice and internal modes.

The LD model is used for the calculation of the contributions to $\alpha(V)$ from phonons of different energies. The calculation technique is described in Ref. 48 and the results of such calculations are presented in Fig. 4(b), showing that the dominant contribution to the thermal expansion is caused by lattice modes. For example, at 12 K thermal expansion is caused mainly by low-energy phonons of acoustic origin. With increasing temperature, contributions to $\alpha(V)$ of modes with energies around 20 and 40 meV are quite significant and as temperature increases these modes become more populated, contributing to the volume thermal expansion significantly. Contributions from internal modes of the MoO_4^{-2}

FIG. 5. (Color online) Thermodynamic properties of CaMoO_4 (per formula unit).

tetrahedron are much smaller, which indicates the structural stability of such complexes.

Thermodynamic properties (heat capacity at constant volume C_V and entropy S) were obtained from the total PDOS $g(\nu)$ using the following equations:

$$C_V(T) = RnN \int_0^\infty g(\nu) \left(\frac{h\nu}{k_B T} \right)^2 \frac{\exp\left(\frac{h\nu}{k_B T}\right)}{\left[\exp\left(\frac{h\nu}{k_B T}\right) - 1 \right]^2} d\nu,$$

$$S(T) = RnN \int_0^\infty g(\nu) \int_0^T \frac{1}{T} \left(\frac{h\nu}{k_B T} \right)^2 \frac{\exp\left(\frac{h\nu}{k_B T}\right)}{\left[\exp\left(\frac{h\nu}{k_B T}\right) - 1 \right]^2} dT d\nu, \quad (10)$$

where h , k_B , and R are the Planck, Boltzmann, and universal gas constants, respectively, n is the number of atoms in the formula unit, and N is the number of formula units in a cell. Thermal dependencies of heat capacity at a constant volume and entropy are shown in Fig. 5. Additionally, heat capacity at constant pressure was calculated using

$$C_P = C_V \left(1 + \frac{\alpha_V^2 K_T T}{\rho} \right). \quad (11)$$

The calculated thermodynamic properties show nearly typical behavior: C_P reaches the classical value $3RnN$ just around 800 K.

D. Debye temperature

Previous considerations of bulk and shear moduli, as well as thermodynamic properties, make possible the estimation of the Debye temperature. As stated above, the classical Debye theory is unable to offer a comprehensive description of the phonon spectrum of CaMoO_4 that is similar to what has been found for calcium tungstate¹⁹ and other complex oxides.^{49–52} Nonetheless, the Debye temperature is an important characteristic that allows the thermodynamic properties

of solids to be characterized in the low-temperature range, where vibrations have an acoustic origin. To the best of our knowledge, no assessment of the Debye temperature for CaMoO₄ has been done hitherto.

Usually two techniques for determining the Debye temperature are employed: θ_D may be calculated from the sound velocities (elastic modules) using the Robie and Edwards equation⁵³ (“elastic” θ_D) or by fitting the thermodynamic properties of materials using the Debye-like interpolation formula (“thermal” θ_D). In the present study the Debye temperature was determined using both approaches. Using the Robie and Edwards equation and average bulk and shear moduli from Refs. 27, 31, and 42–44, the Debye temperature was estimated as 438 ± 2 K. The value of θ_D obtained from the calculated K and G is equal to 446 K, demonstrating good agreement. Lattice heat capacity C_V and lattice entropy S were calculated precisely for the temperature region 0–30 K with 1 K steps and the Debye temperature in the low-temperature limit was determined from the plateaus of the C_V/T^3 and S/T^3 plots as being equal to 395 ± 9 K. Thus one can see a noticeable difference between Debye temperatures obtained using different approaches. The elastic θ_D is higher than the thermal one. This difference would become more pronounced if one were to use the low-temperature elastic data; as, in general, the elastic θ_D values increase as temperature decreases. The reason for such a discrepancy is not well understood. Discussions have begun a long time ago and for better insight into this problem we would like to point the reader to the excellent review of Blackman.⁵⁴ It should be noted that originally the Robie and Edwards equations have been developed for cubic crystals and that such a discrepancy has been initially observed.

E. Grüneisen parameter

Lattice anharmonicity, which leads to a volume dependence of phonon frequencies $\nu_{i,\vec{k}}$ (at the i th mode and at the $\vec{k}$ wave vector) is described by the mode Grüneisen parameter

$$\gamma_{i,\vec{k}} = - \frac{\partial \ln(\nu_{i,\vec{k}})}{\partial \ln(V)} \quad (12)$$

and the thermodynamic Grüneisen parameter defined as a weighted average of the mode Grüneisen parameters

$$\Gamma = \frac{\sum_{i,\vec{k}} \gamma_{i,\vec{k}} C_{i,\vec{k}}}{\sum_{i,\vec{k}} C_{i,\vec{k}}} = \frac{\sum_{i,\vec{k}} \gamma_{i,\vec{k}} C_{i,\vec{k}}}{C_V}, \quad (13)$$

where $C_{i,\vec{k}}$ is the contribution of the i th mode at the $\vec{k}$ wave vector to the total isochoric heat capacity. The thermal dependence of the Grüneisen parameter calculated from Eq. (13) is presented in Fig. 6.

In this, we considered all components, affecting the volumetric thermal expansion coefficient. It is interesting now to make an assessment of the accuracy of the model by comparing the results of the calculations and experiments for thermal expansion. The thermal dependence of the cell vol-

FIG. 6. Calculated thermal dependence of thermodynamic Grüneisen parameter.

ume was reconstructed from the calculated TEC using the P - V equation of state Eq. (5) with $a(T_0)$ and $c(T_0)$ values listed in Table III. The calculated thermal dependence of the cell volume, presented as a solid line in Fig. 2, is in good agreement with the experimentally observed results, thereby justifying the correctness of model and approximations made.

V. CONCLUSIONS

In this work the crystal structure of CaMoO₄ over the temperature range 12–300 K has been studied by x-ray high-resolution powder diffraction using synchrotron radiation. Within the accuracy of the experimental technique used it can be concluded that in the temperature region of interest calcium molybdate belongs to a scheelite type of structure and exhibits no structural anomalies. Our experimental data together with the high-temperature data of Deshpande and Suryanarayana⁴⁰ were used to derive the parameters of anisotropic thermal expansion of the lattice. It is found that TEC along the [001] direction is approximately twice that in the [100] direction of the tetragonal cell.

Thermodynamic properties and LD of calcium molybdate have been investigated using self-consistent semiclassical simulations based on the quasiharmonic approximation and free energy minimization. Compared with the previously reported simulations of LD in CaWO₄ the model was improved by defining the inter- and intramolecular forces that are responsible for interaction *between* and *within* complex anions MoO₄²⁻. The validity of the model and simulations undertaken was verified, where possible, by comparing the number of calculated parameters of the crystal under investigation with those measured in experiment and it was shown that there is a reasonable agreement between them. Based on the improved model of interactions the thermal dependencies of isothermal elastic modules K_T and G_T , heat capacities C_V and C_P , entropy S , thermal expansion, and the Grüneisen parameter, as well as PDOS were calculated and analyzed. From the temperature dependencies of C_V and S we also calculated the Debye temperature ($\theta_D = 395 \pm 9$ K) and

showed that this value is 13% lower than that derived from the elastic constants. As a result of this study it was confirmed that the chosen modeling technique can be successfully applied as a method for calculating the thermal properties of CaMoO_4 crystals over a wide range of temperatures. It is also helpful to understand the various phonon contributions to the total thermal expansion, which facilitates the interpretation of the experimental results. And last but not least: the obtained knowledge on the low-temperature properties and numerical parameters of CaMoO_4 will be used in our R&D of this material for cryogenic phonon scintillation detectors applications.

ACKNOWLEDGMENTS

This work was supported by a grant from the Royal Society (London) “Quest for cryogenic phonon-scintillation detectors: material characterization” between the University of Oxford and Lviv Polytechnic National University and in part by PPARC Grant No. PPA/I/S/2001/00646 and by Ukrainian Ministry of Education and Science (project “Cation”). A. Senyshyn gratefully acknowledges the financial support from the Deutscher Akademischer Austauschdienst (German Academic Exchange Service). Also, we would like to thank Professor J. D. Gale for providing us the GULP code.

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