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Crystalline electric field and lattice contributions to thermodynamic properties of PrGaO₃: specific heat and thermal expansion

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Abstract

The low-temperature heat capacity of perovskite-type PrGaO₃ has been measured in the temperature range from 2 to 320 K. Thermodynamic standard values at 298.15 K are reported. An initial Debye temperature $\theta_D(0) = (480 \pm 10)$ K was determined by fitting the calculated lattice heat capacity. The entropy of the derived Debye temperature functions agrees well with values calculated from thermal displacement parameters and from atomistic simulations. The thermal expansion and the Grüneisen parameter, arising from a coupling of crystal field states of Pr³⁺ ion and phonon modes at low temperature, were analysed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Perovskite-type rare-earth (Ln) gallates with stoichiometry LnGaO₃ have attracted the attention of researchers for a long time. These materials are useful substrates for giant magnetoresistance manganate, Pb(Sr)TiO₃, GaN and high-temperature cuprate superconductor films, for which buffer layers are not obligatory. Just recently [1], a new kind of electrolyte for solid oxide fuel cells based on LaGaO₃ perovskite oxide doped with Sr and Mg was established. Later, this effect was tested on other LnGaO₃ and LnAlO₃ doped with alkaline-earth elements. High oxide-ion conductivity of similar magnitude to that for doped LaGaO₃ has been reported for doped PrGaO₃ [2, 3], rendering the material suitable for electrolytes in solid oxide fuel cells.

The development of applications based on these materials requires precise knowledge of their crystal structure, its thermal evolution and accompanying properties. The first report on the structure of PrGaO_3 was given in 1954 by Ruggiero *et al* [4], who reported the ‘ideal’ ($Pm\bar{3}m$ space group) perovskite structure for this compound. Later, Marezio *et al* found the GdFeO_3 structure type ($Pbnm$) and attributed it for all LnGaO_3 (except PmGaO_3) at room temperature [5]. For more than 25 years, only crystal structure data at room temperature and information about possible phase transformations were available. In the early 1990s these materials were mainly evaluated as substrates for superconducting cuprate films [6–9]. In 1994 Marti *et al* [10] reported structure parameters at 12 K for three LnGaO_3 ($\text{Ln} = \text{La}, \text{Pr}$ and Nd) and high-temperature (413, 573, 1353 and 1673 K) structural data for LaGaO_3 . The latter authors found the GdFeO_3 type of structure for PrGaO_3 and that the cell size in the [010] direction at 12 K is larger than that at room temperature.

In our recent investigations we studied the thermal evolution of structural properties for the set of LnGaO_3 and their solid solutions. A strong anisotropy of thermal expansion has been observed for $\text{La}, \text{Ce}, \text{Pr}$ and Nd gallates [11–14], but for PrGaO_3 an anisotropic (in the sense reported by Marti *et al* [10]) and an even volumetric contraction of the cell has been observed at low temperatures [11, 14]. A similar behaviour is also found for $\text{La}(\text{Pr})\text{GaO}_3$ [15] and $\text{Nd}(\text{Pr})\text{GaO}_3$ (unpublished) solid solutions, whereas no indications for negative thermal expansion was detected in LnGaO_3 and their solid solutions without praseodymium.

An excellent review on different negative thermal expansion mechanisms is presented in [16]. In simple structures [17] negative thermal expansion is accompanied by bond compression, whereas, for example, in complex oxides [18] a mixture of bond compression and rotation of polyhedra is expected. The above-mentioned features, however, cannot explain the observed uniqueness of the Pr ion in LnGaO_3 . Thus, the mechanism should be connected to the properties of Pr ion in the LnGaO_3 matrix, particularly in the interactions between phonons and the electronic subsystem. The trivalent praseodymium ion $\text{Pr}^{3+}(4f^2)$ has a ground multiplet term 3H_4 which splits under the influence of a crystal electric field (CEF). It is well known that the thermal and magnetic properties of 4f-element-containing materials display anomalies caused by CEF–electronic subsystem interactions. The first attempt to study the CEF splitting in PrGaO_3 was made by Feldmann *et al* [19] using inelastic neutron scattering. Similar studies were performed later by Podlesnyak *et al* [20] and several inelastic peaks of magnetic origin in an energy transfer range below 86 meV were analysed. Negative thermal expansion caused by crystal field splitting has been reported for different rare-earth compounds such as antimonides [21], cuprates [22] and oxides [23, 24]. In [25] we announced low-temperature anisotropic negative thermal expansion for perovskite-related TmCaAlO_4 ; similar anomalies were observed for isostructural ErAlO_3 [26] and TbAlO_3 [27]. Just recently, a set of crystal-field-driven structural phase transformations has been reported for CeAlO_3 and $\text{Ce}_{1-x}\text{Ln}_x\text{AlO}_3$ ($\text{Ln} = \text{La}, \text{Nd}$) solid solutions [28].

The present work is part of our systematic studies of the thermal properties of LnGaO_3 and makes use of the information included in the temperature dependence of the heat capacity—which is an integral description of the phonon spectrum. In this work, attempts to separate the influences caused by anharmonicity and CEF as well as to test the force-field model for simulations have been made.

2. Experimental setup

An ingot of PrGaO_3 was grown by the Czochralski method at the Institute of Physics, Warsaw, Poland [29] and was cut into pieces. Powder diffraction studies confirmed that only the GdFeO_3 type of structure is present. For heat capacity measurements, a flat single-crystalline

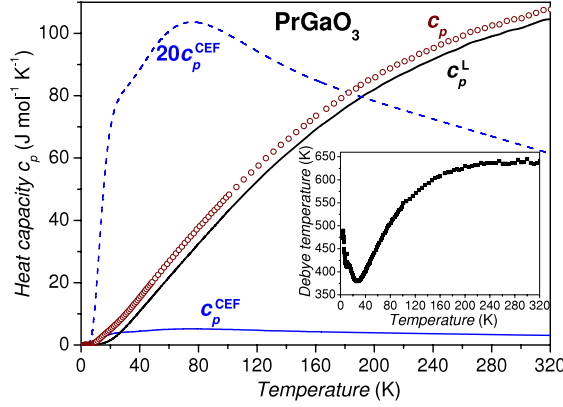


Figure 1. Temperature dependence of the molar heat capacity c_p (circles), the calculated crystal electric field contribution c_p^{CEF} (—, 20 fold magnification - - -), and the derived lattice contribution c_p^{L} (—). The inset illustrates the temperature dependence of Debye temperature.

piece (13.781(1) mg) was mounted onto the sample holder platform with a small amount (0.026(1) mg) of Apiezon N grease. The calorimeter (PPMS, Quantum Design) uses a relaxation method. The heat capacities of the sample holder, determined in a separate run, and of the grease [30] were subtracted from the total measured heat capacity. The uncertainty in the molar heat capacity $c_p(T)$ has been found to be about 1% between 1.8 and 50 K, and increases to 1.5% at 320 K.

3. Results and discussion

3.1. Heat capacity

The molar heat capacity $c_p(T)$ of PrGaO_3 is plotted in figure 1. By numerical integration of the experimental data, the following thermodynamic standard values are obtained: $c_p(298.15 \text{ K}) = 104.9(2.0) \text{ J mol}^{-1} \text{K}^{-1}$, $S(298.15 \text{ K}) = 120.0(1.2) \text{ J mol}^{-1} \text{K}^{-1}$, and $H(298.15 \text{ K}) = 18.5(2) \text{ kJ mol}^{-1}$.

In the insulating rare-earth gallates, two terms add to the observed molar heat capacity $c_p(T)$: the lattice heat capacity $c_p^{\text{L}}(T)$ and the crystalline electric field (CEF) contribution $c_p^{\text{CEF}}(T)$, thus $c_p = c_p^{\text{L}} + c_p^{\text{CEF}}$. Due to the well-isolated singlet of the CEF ground state, the Pr^{3+} ions do not order magnetically in PrGaO_3 . In order to separate the influences, the CEF contribution is calculated according to the multilevel Schottky scheme for a $^3\text{H}_4$ system (with nine levels):

$$c_p^{\text{CEF}} = \left(\frac{\partial U}{\partial T} \right)_V = k_B \left[\sum_{i=1}^9 \left(\frac{E_i}{k_B T} \right)^2 p_i - \sum_{i=1}^9 \left(\frac{E_i}{k_B T} p_i \right)^2 \right], \quad (1)$$

where $p_i = Z^{-1} \exp\{-E_i/k_B T\}$ is the Boltzmann population factor, $Z = \sum_i \exp(-E_i/k_B T)$ is the partition function, k_B is the Boltzmann constant, and E_i are the CEF energy levels. Values E_i for the calculation of c_p^{CEF} of PrGaO_3 were obtained from inelastic neutron scattering [20]: singlets were at $E_1 = 0$, $E_2/k_B = 59.2 \text{ K}$, $E_3/k_B = 185.7 \text{ K}$, $E_4/k_B = 249.5 \text{ K}$, $E_5/k_B = 441.0 \text{ K}$, $E_6/k_B = 782.2 \text{ K}$, and $E_7/k_B = 804.2 \text{ K}$. The two remaining levels at 995.7 and 1312.5 K were neglected in the calculation. For an optimum fit to our data the lowest

exited level had to be set to 58.0 K. The temperature dependences of the observed experimental molar heat capacity c_p , the calculated c_p^{CEF} , and the derived lattice contribution c_p^{L} are presented in figure 1.

The equivalent Debye temperature $\theta_D(T)$ has been calculated from the lattice term $c_p^{\text{L}}(T)$ supposing that $c_V^{\text{L}} \approx c_p^{\text{L}}$ at low temperatures. The calculated temperature dependence of θ_D (shown in the inset) exhibits typical behaviour [31]: the initial thermal Debye temperature for PrGaO₃ of $\theta_D(0) = 480 \pm 10$ K has been determined; then the $\theta_D(T)$ decreases with increasing T and a minimum of 378 K is observed at 27 K; at higher temperatures the difference between c_V^{L} and c_p^{L} grows too large. The Debye temperature θ_D can also be estimated from the temperature dependence of the atomic displacement parameters (ADP). Using ADP values obtained from Rietveld refinement of synchrotron powder diffraction data [14] and the methodology developed in [32, 33], we obtained the Debye temperature $\theta_D^{\text{ADP}} = 497 \pm 32$ K. This value agrees with the initial thermal value $\theta_D(0)$ within the uncertainty limits. Similar estimates were made in [13] for NdGaO₃ ($\theta_D^{\text{ADP}} = 510 \pm 27$ K). The observed relatively large deviations are primarily caused by the low accuracy in the determination of the ADP from x-ray powder diffraction data. From atomistic simulations of PrGaO₃ [34] with the General Utility Lattice Program [35], the Debye temperature at room temperature is estimated to be $\theta_D = 548$ K. For the details of simulations we refer to publications describing simulations of perovskite-like materials [13, 34, 36, 37] as well as of some other complex oxides [38, 39].

One typical feature has been observed for all rare-earth perovskite-type gallates in the course of simulations—they cannot be treated as a proper Debye like solids. The shape of calculated phonon density of states (PDOS) does not reproduce the parabolic law of the phonon dispersion assumed in the 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 PDOS, determined by relative masses and the number of atoms of each sort. In [34] we also reported on the unsuccessful attempts to reproduce a negative thermal expansion effect in PrGaO₃. From the analysis of structural and thermodynamical parameters obtained during free-energy minimization procedure, no reasons for negative expansion have been found. We associated the failure of the atomistic technique to the possible influences of electronic effects, for which simulations with the semi-classical approach have been found incapable.

From the known PDOS [34], the temperature dependence of the lattice heat capacity at constant volume $c_V^{\text{L}}(T)$ could be obtained easily by integration over all frequencies. The isochoric $c_V^{\text{L}}(T)$, along with the isobaric $c_p^{\text{L}}(T)$, are presented in figure 2. An encouraging agreement is observed which indicates the correctness and accuracy of the chosen model of interactions. At low temperatures the agreement is good but, with increasing temperature, differences between the curves become more pronounced, in agreement with the well-known relationship $c_p = c_V(1 + \alpha\gamma T)$, where α is the volume thermal expansion coefficient and γ is the Grüneisen parameter.

3.2. Thermal expansion

With known lattice and CEF contribution to heat capacity, let us estimate their contributions to the thermal expansion of PrGaO₃. The volume thermal expansion coefficient α_V in the quasi-harmonic approximation can be written as

$$\alpha_V = \frac{\gamma \rho c_V^{\text{L}}}{K_T} = \frac{\gamma \rho c_p^{\text{L}}}{K_S}, \quad (2)$$

where γ is the Grüneisen parameter, ρ is the mass density of the material, and K_T and K_S are isothermal and adiabatic bulk modules, respectively. In most cases, the phonon–phonon

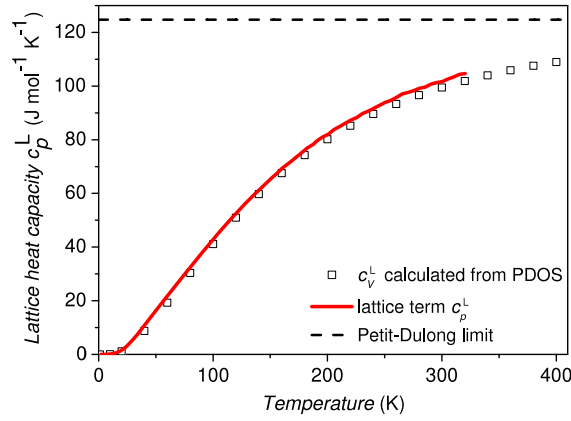


Figure 2. Temperature dependence of the lattice heat capacity c_p^L (solid line: calculated from $c_p - c_p^{\text{CEF}}$), for the lattice heat capacity at constant volume c_V (squares: calculated by PDOS integration). The dashed line marks the Petit–Dulong value $3nR$ (number of atoms $n = 5$).

interactions dominate the thermal expansion coefficient α_V in a solid. However, similar to the heat capacity, α_V can be described by the sum of different contributions, e.g. lattice, magnetic, electronic etc, or in this case

$$\alpha_V = \alpha_V^L + \alpha_V^{\text{CEF}}. \quad (3)$$

The total thermal expansion coefficient α_V has been determined using the relation $\alpha(T) = \partial \ln(V(T))/\partial T$, where $\alpha(T)$ was calculated from the recently reported thermal dependence of cell volume $V(T)$ [11, 14] obtained by high-resolution powder diffraction and synchrotron radiation.

The ‘lattice’ thermal expansion α_V^L can be estimated either by using the thermal dependence of $V(T)$ of similar nonmagnetic perovskites (e.g. LaGaO_3 , LuGaO_3) or from atomistic simulations. From the viewpoint of a good agreement between experimental and calculated lattice heat capacities, calculations of the thermal behaviour of the cell volume seems to be a promising approach. Using $V(T)$ for the nonmagnetic perovskite LaGaO_3 [11] does however not result in significant changes and improvements. Therefore, for greater clarity, in the calculation of α_V^L the volume of the relaxed cell of PrGaO_3 [34] was utilized for $V(T)$.

The experimental $\alpha_V(T)$ and the calculated $\alpha_V^L(T)$ are presented in figure 3. The temperature dependence of the additional thermal expansion coefficient contribution $\alpha_V^{\text{CEF}}(T)$ is shown in the inset by the circles.

There is a clearly visible negative peak in $\alpha_V^{\text{CEF}}(T)$ with a minimum at ≈ 45 K. From equation (2) it is evident that negative values of the thermal expansion coefficient can be accumulated only in the value of the Grüneisen parameter (which is a measure of the lattice anharmonicity). In contrast to the heat capacity and thermal expansion coefficient, the Grüneisen parameter is not an additive property:

$$\gamma = \frac{\gamma^L c_p^L + \gamma^{\text{CEF}} c_p^{\text{CEF}}}{c_p} = \frac{\gamma^L c_V^L + \gamma^{\text{CEF}} c_V^{\text{CEF}}}{c_V}, \quad (4)$$

where $\gamma^{(i)}$ can be calculated from the density, lattice and CEF thermal expansion coefficients, heat capacities and bulk modules as $\gamma^{(i)} = \alpha^{(i)} K_S / (c_p^{(i)} \rho) = \alpha^{(i)} K_T / (c_V^{(i)} \rho)$.

Having known thermal expansion coefficients and heat capacities, the temperature dependence of bulk modules is required for further determination of the Grüneisen parameters.

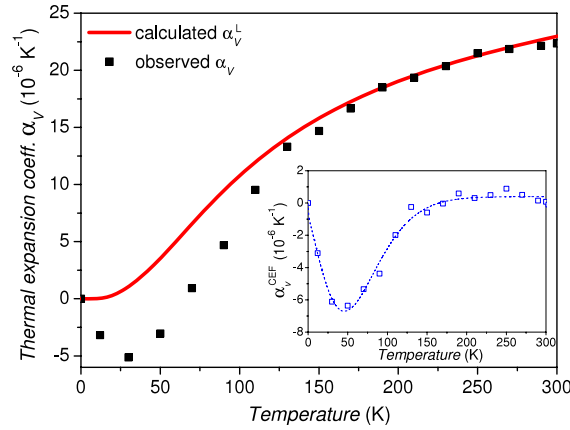


Figure 3. Thermal expansion coefficient of PrGaO₃ versus temperature. The inset illustrates the difference curve $\alpha_V^{\text{CEF}} = \alpha_V - \alpha_V^L$, the dashed line is a guide to the eye.

Neglecting the possible CEF contributions to K_T and K_S , the temperature dependence of the isothermal bulk modules has been obtained from semiclassical simulations [34]. The calculated K_T decreases smoothly from 191.4 GPa in the low-temperature limit to 189.8 GPa at 300 K, which is in good agreement with $K_T = 190$ GPa for neodymium gallate obtained from acoustic measurements at 77 K [40]. To determine the temperature dependence of adiabatic bulk modules, the renormalization procedure, $K_S = K_T c_p^L / c_V^L$, has been applied. The calculated Grüneisen parameters $\gamma^{(i)}$ are shown in figure 4(a). The lattice Grüneisen parameter, γ^L , remains practically independent of temperature, whereas the total and the CEF Grüneisen parameters display pronounced temperature dependences. In the limit $T \rightarrow 0$, the thermal expansion coefficient and the heat capacity converge towards zero and the γ s show an asymptotic behaviour associated with diminishing anharmonicity and with increased indeterminacy at low temperatures. Under the stimulus of warming, both γ and γ^{CEF} increase, and at around 60 K the total Grüneisen parameter γ becomes equal to zero. The CEF Grüneisen parameter γ^{CEF} increases like γ . Above 150 K the influence of the CEF term becomes equal to zero within uncertainty and $\gamma \approx \gamma^L$. The observed behaviour of the Grüneisen parameters correlates well with the respective behaviour for the lattice parameter in the [010] direction of the orthorhombic lattice. The temperature behaviour of the b lattice parameter [11, 14] is plotted in figure 4(b), together with the temperature dependence of the cell volume in perovskite-type PrGaO₃.

Despite the negative volumetric thermal expansion being limited to about 60 K (64 K obtained from the derivative of $V(T)$), the CEF influence remains significant up to about 150 K (166 K obtained from the derivative of $b(T)$). However, at higher temperature, no influence of the CEF on the structural properties of PrGaO₃ can be discerned.

4. Conclusions

The molar heat capacity of perovskite-type PrGaO₃ has been studied by low-temperature calorimetry between 2 and 320 K. The measured molar heat capacity was separated into the lattice heat capacity and the Schottky contribution due to the crystal field splitting of the Pr³⁺ ions ³H₄ ground multiplet. The Debye temperature was calculated from the lattice heat capacity and entropy, and has been found to be in good agreement with the values obtained from displacement parameters and atomistic simulations.

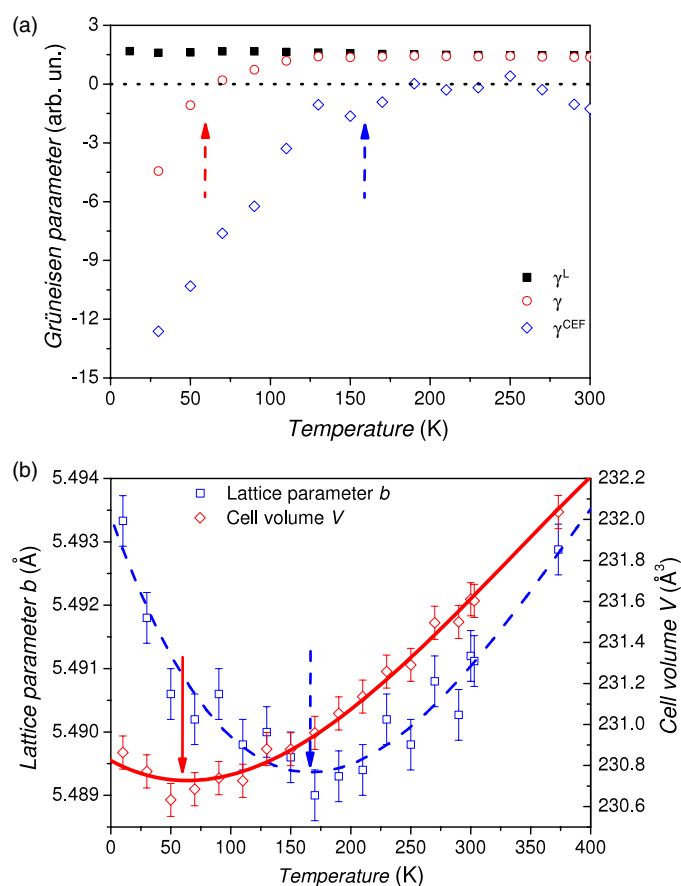


Figure 4. Temperature dependence of the Grüneisen parameters $\gamma^{(i)}$ for the lattice, crystal field and overall contributions (a) and thermal dependencies of the b lattice parameter and cell volume V taken from [11, 14] (b). Lines are guides for the eyes.

A possible mechanism for negative thermal expansion was proposed, motivated by a comparison of the observed and calculated (within a semi-classical approach) properties. The results of simulations agree well with the observed structural anomalies.

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