

## Specific heat of the elpasolite $\text{Pb}_2\text{MgWO}_6$

I. N. Flërov\*<sup>1)</sup> and M. V. Gorev

*L. V. Kirenskii Institute of Physics, Siberian Branch, Russian Academy of Sciences,  
660036 Krasnoyarsk, Russia*

Ph. Sciau

*Centre d'Elaboration des Matériaux et d'Etudes Structurales, CNRS, 31055 Toulouse, France  
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The specific heat of  $\text{Pb}_2\text{MgWO}_6$  has been measured in the temperature interval 83–370 K. An anomaly in the specific heat associated with the phase transition at  $T_0 = 312.8$  K has been discovered. The thermodynamic parameters of the structural phase transition  $Fm3m - Pmcn$  have been determined. © 1999 American Institute of Physics. [S1063-7834(99)03209-8]

There exists a wide class of oxygen compounds with general formula  $\text{A}_2\text{BB}'\text{O}_6$ , which undergo structural phase transitions of diverse nature, including transitions associated with compositional ordering of the cations B and B'. The degree of ordering of the cations has a substantial affect both on the physical properties of the compound and on the nature of the structural transformations taking place in it.<sup>1</sup> The temperature of compositional ordering is determined, first of all, by the difference in the charges and dimensions of the ordering ions.  $\text{Pb}_2\text{B}^2\text{WO}_6$  compounds, as a rule, are ordered mainly due to the significant difference in the charges of the  $\text{B}^{2+}$  and  $\text{W}^{6+}$  ions and in the high-temperature phase have elpasolite structure (an ordered perovskite, space group  $Fm3m$ ).<sup>1</sup> Depending on the size of the  $\text{B}^{2+}$  ion in these compounds, distorted phases of varied symmetry can be realized by a change in the temperature. Elpasolite with Mg as the B ion undergoes transitions to the antiferroelectric state,<sup>2</sup> which is preceded in the compound having Co as the B ion by an incommensurate phase in a wide temperature interval.<sup>3</sup> Substitution of the cobalt ion by cadmium leads to a substantial growth in the temperature of loss of stability of the original cubic phase.<sup>4</sup>

Despite active research into oxygen elpasolites by various methods, detailed information about their thermodynamic properties and their behavior during phase transitions are lacking. What information about them exists was obtained for isolated representatives of the family and, as a rule, using a differential scanning calorimeter; only in Ref. 5 was  $\text{Pb}_2\text{MgWO}_6$  investigated using an adiabatic calorimeter, but only in a limited temperature interval (275–311 K) in the vicinity of the phase transition at  $T_0 = 303.5$  K. At the same time, from the temperature dependence of the relative elongation and volume,<sup>2,6</sup> it follows that additional thermodynamic parameters associated with the phase transition (thermal expansion coefficient, specific heat) should be present over a significant wider temperature interval. Reference 5 investigated a ceramic material in which, so the authors maintained, the existence of an inhomogeneous composition is possible. It is entirely possible that this is precisely the reason the temperature of the phase transition in this sample<sup>5</sup>

proved to be lower than its value determined in other studies (312 K, Ref. 1). The structure of the initial cubic phase and the distorted phase of  $\text{Pb}_2\text{MgWO}_6$  was resolved in Ref. 7. The symmetry of the low-temperature phase turned out to be orthorhombic with space group  $Pmcn$ . In a Raman light-scattering study on a powder sample of  $\text{Pb}_2\text{MgWO}_6$ , a soft mode was discovered in the  $Pmcn$  phase, condensing in the center of the Brillouin zone.<sup>8</sup> This gave cause to believe that a phase transition of displacement type is realized in this compound. At the same time, the diffuse Raman signal observed in the cubic phase indicated that there is also a contribution to the mechanism of the phase transition from phenomena apparently associated with ordering of lead and oxygen atoms,<sup>8</sup> which according to the structural studies are disordered in the cubic phase over several local sites.<sup>7</sup>

The Raman scattering spectra and the dielectric constant were later examined in greater detail in single-crystal  $\text{Pb}_2\text{MgWO}_6$  (Ref. 9). The results of this study confirm the hypothesis made in Ref. 8 of a double mechanism of this phase transition. On the other hand, it is asserted that there exists in this compound a phase intermediate between the cubic paraelectric phase and the orthorhombic antiferroelectric phase, and a second phase transition occurs in the region 220–240 K.

The present paper reports a careful study of the specific heat of elpasolite  $\text{Pb}_2\text{MgWO}_6$  over a wide temperature range with the aim of elucidating the nature of its behavior and determining its thermodynamic parameters such as the existence interval of the excess specific heat, entropy difference, and hysteresis of the phase transition temperature.

Specific-heat measurements were performed on the powder sample used earlier in experiments to refine the structure of the compound<sup>7</sup> and in the Raman light scattering studies.<sup>8</sup> An analysis of the x-ray diffraction patterns showed that impurities are absent in the sample which would have come from the initial ingredients used in the solid-state synthesis, and that foreign phases are absent as well.<sup>8</sup> It was also established that disorder is absent in the distribution of  $\text{Mg}^{2+}$  and  $\text{W}^{6+}$  ions occupying the sites at the centers of the corresponding octahedra.<sup>7</sup> The sample in powdered form pos-

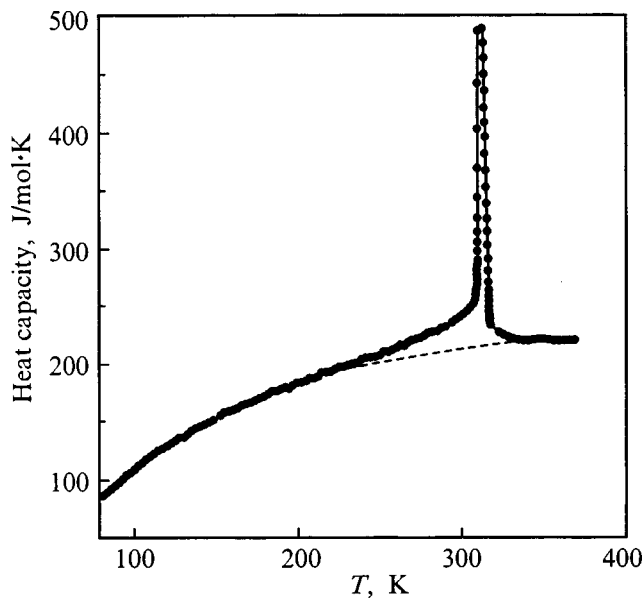


FIG. 1. Temperature dependence of the specific heat of  $\text{Pb}_2\text{MgWO}_6$ . The dashed curve is the lattice specific heat.

sesses the advantage that it is free of the mechanical stresses which inevitably arise in a ceramic during hot pressing.

The specific heat was examined in the interval 83–370 K with the use of an adiabatic calorimeter in the regimes of discrete and continuous heating/cooling. A powder sample of  $\text{Pb}_2\text{MgWO}_6$  with mass 4.297 g was placed in an indium container which was sealed in a helium atmosphere. Below 300 K the measurements were performed using a liquid-nitrogen bath, and in the interval 290–370 using an ice bath. The temperature regions of the phase transitions were examined with the help of low-static thermograms with low rates of variation of temperature  $dT/dt = \pm 4 \times 10^{-4}$  K/s.

Results of the measurement of the specific heat  $C_p(T)$  are plotted in Fig. 1. One specific-heat anomaly is revealed, with a maximum at  $313.1 \pm 0.5$  K.

Figures 2a and 2b present results of a specific-heat measurement in the temperature region where some peculiarities in the Raman spectra and in the behavior of the dielectric constant were observed in Ref. 9 and interpreted as being associated with a second phase transition in  $\text{Pb}_2\text{MgWO}_6$ . The relatively small and uniform spread of the experimental points from the smoothed curve of  $C_p(T)$ , both in the series of continuous heating and in the series of discrete heating, allows us to state unambiguously that there are no anomalies in the specific heat in the investigated sample in the temperature interval 200–250 K, at least within the limits of  $1.0 \text{ J/mol}\cdot\text{K}$ , which amounts to 0.5% of the total specific heat of the compound.

Thermographic studies of temperature regions centered on the phase transition  $Fm3m - Pmcn$  allowed us to refine the transition temperature to  $T_0 = 312.8 \pm 0.2$  K, which is in satisfactory agreement with the data of Ref. 2, and also enabled us to determine its hysteresis  $\delta T_0 = 2.45 \pm 0.2$  K (Fig. 3). From the thermograms we also calculated the latent heat (or jump in the enthalpy at the phase transition), which is equal to  $\delta H_0 = 2340 \pm 200 \text{ J}\cdot\text{mol}^{-1}$ , and the

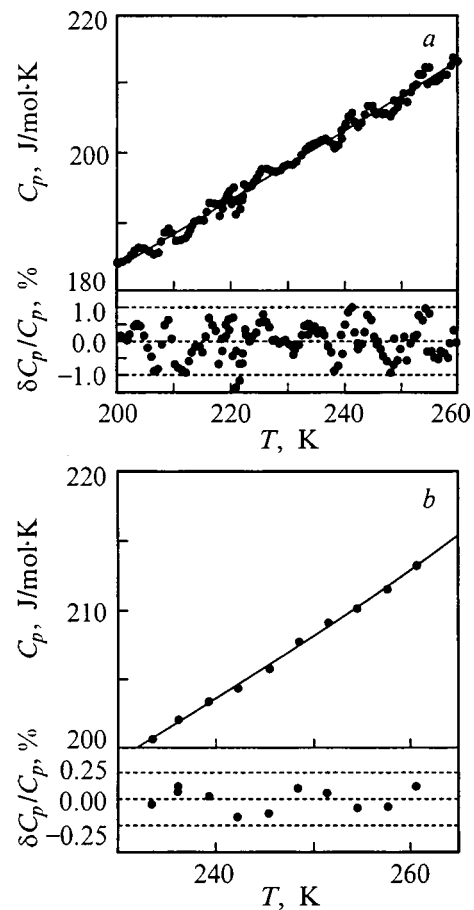


FIG. 2. Specific heat of  $\text{Pb}_2\text{MgWO}_6$  in the region of the second phase transition suggested in Ref. 9, measured using the methods of continuous (a) and discrete (b) heating, with deviations of the experimental points from the corresponding smoothed curves.

corresponding change in the entropy  $\delta S_0 = \delta H_0 / T_0 = 7.48 \pm 0.52 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . The quantities  $\delta H_0$  and  $\delta T_0$  in the sample investigated in this study turned out to be two times larger than the values obtained in Ref. 5. This also testifies on behalf of a higher degree of perfection of the powder sample in comparison with a ceramic sample since a decrease in  $\delta H_0$  and  $\delta T_0$  from one sample to another of the same compound  $\text{A}_2\text{BB}'\text{O}_6$  can be due to a “washing out” of the phase transition as a consequence of the presence in the sample of significant mechanical stresses and/or a disruption of the degree of ordering of the B and B' ions.

The effect of hydrostatic pressure on the anomaly in the dielectric constant at the phase transition in  $\text{Pb}_2\text{MgWO}_6$  was investigated in Refs. 10 and 11. The data of different authors differ quite significantly:  $dT_0/dp = -0.59$  (Ref. 10) and  $-0.38 \text{ K/GPa}$  (Ref. 11). Using this information and the value of  $\delta S_0$  determined in the present work, it is possible to use the Clapeyron–Clausius equation  $dT_0/dp = (\delta V_0/V) / \delta S_0$  to calculate the jump in the volume at the phase transition point, which turns out to lie within the limits  $(\delta V_0/V) = -(3.7 - 5.7) \times 10^{-3}$  for the two values of  $dT_0/dp$  corresponding to the data of Refs. 11 and 10. Experimentally, it has been found that  $(\delta V_0/V) = -2.6 \times 10^{-3}$  (Ref. 11) and  $-4.7 \times 10^{-3}$  (Ref. 6).

To calculate the integral thermodynamic characteristics

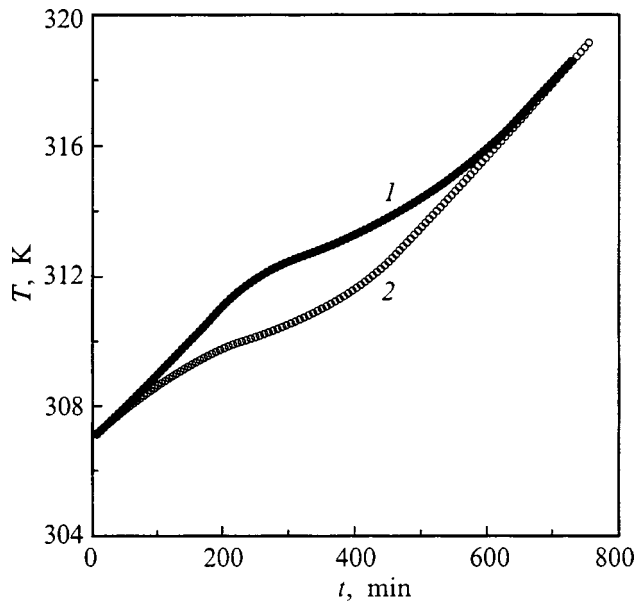


FIG. 3. Thermograms recorded during the heating (1) and cooling (2) in the vicinity of the  $Fm3m-Pm3n$  phase transition in  $Pb_2MgWO_6$ .

of the phase transition between the cubic and orthorhombic phases, it was necessary to separate out the anomalous contribution  $\Delta C_p(T)$ , defined as the difference between the total  $C_p(T)$  and lattice  $C_{lat}(T)$  specific heats. The latter was determined by fitting the experimental data far from the phase transition temperature  $T_0$  by the Debye and Einstein functions  $C_{lat}(T) = A_1 D(\theta_D/T) + A_2 E(\theta_E/T)$  and is represented by the dashed line in Fig. 1. By varying the datasets for the high- and low-temperature phases included in the processing, we determined optimal values of the constants  $A_1 = 391.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}$ ,  $A_2 = 113.0 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}$ ,  $\theta_D = 262.3 \text{ K}$ , and  $\theta_E = 552.7 \text{ K}$ . The temperature interval in which the anomalous specific heat occurs turned out to be quite wide: from 200 to 345 K, which is in satisfactory agreement with the thermal expansion data of Ref. 6.

The excess entropy of the phase transition was calculated by integrating the function  $(\Delta C_p/T)(T)$ . The total entropy difference associated with the phase transition is  $\Delta S_0 = 13.00 \pm 1.05 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ . The ratio  $\delta S_0/\Delta S_0 = 0.58$  indicates that the  $Fm3m-Pm3n$  phase transition in  $Pb_2MgWO_6$ , although first order, is quite close to the tricritical point.

While refining the structure of the cubic phase, we no-

ticed that the best values of the various  $R$ -factors correspond to the situation where the lead atoms are disordered over several equivalent sites.<sup>7</sup> At the same time, these quantities turned out to be very similar to each other for the possible displacements of the lead atoms in the  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 111 \rangle$  directions leading to 6, 12, and 4 equivalent sites, respectively. In the orthorhombic phase, along with small rotations and weak distortions of the octahedra, we indeed discovered a displacement of the lead atoms along the  $[010]_p$  axis of the pseudocubic cell. Thus, the structural data suggest that the contribution to the entropy difference associated with the  $Fm3m-Pm3n$  phase transition in  $Pb_2MgWO_6$  due to ordering of the lead atoms should be  $\Delta S/R = \ln 6 = 1.79$ . The entropy difference determined in the present work,  $\Delta S_0/R = 1.56 \pm 0.13$ , turns out to be less than this value, but larger than  $\ln 4$ . As for the change in the entropy due to rotation of the octahedra, this quantity, as was shown in Ref. 12, is not large as a rule.

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<sup>\*</sup>)E-mail: flerov@iph.krasnoyarsk.su

- <sup>1</sup>A. A. Bokov, *Izv. Ross. Akad. Nauk, Ser. Fiz.* **57**(6), 25 (1993).
- <sup>2</sup>G. A. Smolenskiĭ, N. N. Kraĭnik, and A. I. Agranovskaya, *Fiz. Tverd. Tela (Leningrad)* **3**, 981 (1961) [*Sov. Phys. Solid State* **3**, 714 (1961)].
- <sup>3</sup>W. Brixel, M. L. Werk, P. Fischer, W. Bührer, J.-P. Rivera, P. Tissot, and H. Schmid, *Jpn. J. Appl. Phys., Suppl.* **24**(2), 242 (1985).
- <sup>4</sup>Ph. Sciau and D. Grebille, *Aperiodic'94, Proceedings of the International Conference on Aperiodic Crystals* (World Scientific, Singapore, 1994), p. 460.
- <sup>5</sup>B. A. Strukov, K. A. Minaeva, T. L. Skomorokhova, and V. A. Isupov, *Fiz. Tverd. Tela (Leningrad)* **8**, 972 (1966) [*Sov. Phys. Solid State* **8**, 740 (1966)].
- <sup>6</sup>G. Baldinozzi, Ph. Sciau, and P.-A. Buffat, *Solid State Commun.* **86**, 541 (1993).
- <sup>7</sup>G. Baldinozzi, Ph. Sciau, M. Pinot, and D. Grebille, *Acta Crystallogr., Sect. B: Struct. Sci.* **51**, 668 (1995).
- <sup>8</sup>G. Baldinozzi, Ph. Sciau, and A. Bulou, *J. Phys.: Condens. Matter* **7**, 8109 (1995).
- <sup>9</sup>A. Kania, E. Jahfel, G. E. Kugel, K. Roleder, and M. Hafid, *J. Phys.: Condens. Matter* **8**, 4441 (1996).
- <sup>10</sup>I. N. Polandov, *Fiz. Tverd. Tela (Leningrad)* **5**, 1147 (1963) [*Sov. Phys. Solid State* **5**, 838 (1963)].
- <sup>11</sup>N. Yasuda, S. Fujimoto, and T. Yoshimura, *J. Phys. C* **19**, 1055 (1986).
- <sup>12</sup>I. N. Flerov, M. V. Gorev, K. S. Aleksandrov, A. Tressaud, G. Grannec, and M. Couzi, *Mater. Sci. Eng.* **24**, 81 (1998).

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