Experimental Measurement and Calculation of Mole Heat Capacity and Thermodynamic Functions of Wulfenite $PbMoO_4$

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The heat capacity of natural lead molybdate (wulfenite, $PbMoO_4$) has been measured by the method of vacuum adiabatic calorimetry over the temperature range of (55 to 320) K, and its thermodynamic functions have been calculated. The obtained standard values are as follows: $C_p°(298.15) = (119.41 \pm 0.13)$ $J \cdot mol^{-1} \cdot K^{-1}$, $S°(298.15) = (168.33 \pm 2.06)$ $J \cdot mol^{-1} \cdot K^{-1}$, $\Delta H° = (23\,095 \pm 50)$ $J \cdot mol^{-1}$. For extrapolation of heat capacity values to absolute zero, the equation $C(T) = (AT^{-1/\alpha\beta} + 1)^{-1/\alpha}$ has been used, where parameter α is the power at which the heat capacity verges toward the Dulong and Petit limiting value, and parameter β reflects structural anisotropy of the compound and can possess values from 1 to 3. The values of parameters found by means of linearization were $\alpha = 0.61$ and $\beta = 1.9$. An error for the extrapolation data to absolute zero has been estimated based on the results of heat capacity measurements of the isostructural compound calcium tungstate, $CaWO_4$. The values of the wulfenite heat capacity over the range of (0 to 55) K have also been calculated by the semiempirical method MNDO with the help of a program package on quantum-chemical computation (MOPAC) and according to the method of interatomic potentials within the bounds of dynamics of crystal lattice theory using the computer program LADY.

Introduction

Natural lead molybdate (wulfenite, $PbMoO_4$) belongs to minerals occurring in the oxidation zones of lead−zinc deposits, and the mineral is a source of molybdenum and lead. According to its crystallographic structure, wulfenite has a scheelite-type structure. The compounds of this group feature diverse dielectric properties. At the same time, the thermodynamic properties of wulfenite remain comparatively little investigated.

Kelley[1] gives a heat capacity value of $C_p = 127.19$ $J \cdot mol^{-1} \cdot K^{-1}$ for the temperature range from (292 to 322) K. Naumov et al.[2] give the following thermodynamic values: $C_p°(298.15) = 119.7$ $J \cdot mol^{-1} \cdot K^{-1}$, $S°(298.15) = (166.10 \pm 2.09)$ $J \cdot mol^{-1} \cdot K^{-1}$, $\Delta_f G°(298.15) = 948.47$ $kJ \cdot mol^{-1}$, and $\Delta_f H°(298.15) = -1049.05$ $kJ \cdot mol^{-1}$. In this case, the recommended value $\Delta_f G°(298.15)$ does not agree with the value calculated from the experimental magnitude of the activities product exponent, $pL_0 = 9.72$. Robie and Hemingway[3] give the value $S°(298.15) = (166.1 \pm 2)$ $J \cdot mol^{-1} \cdot K^{-1}$, but a value for $C_p°(298.15)$ is absent.

The crystallographic structure of wulfenite is described in previous work.[4,5] Wulfenite belongs to the tetragonal syngony, spatial group $I4_1/a$, and the parameters of the unit cell are $a = 5.4312$ Å and $c = 12.1065$ Å. The number of formula units per unit cell is $Z = 4$, and the total number of atomic positions per entire cell is 24. The crystal structure of wulfenite samples in which molybdenum is partially replaced by tungsten (the isomorphic series wulfenite $PbMoO_4$−stolzite $PbWO_4$) has been considered.[6,7] The wulfenite vibration spectra have also been investigated in detail. Descriptions of infrared spectra and Raman scattering spectra of different samples of the mineral have been presented.[8−14]

Some studies[15−17] should be noted among the low-temperature investigations of compounds that are isostructural with wulfenite. Lyon and Westrum[15] give the results of low-temperature measurements of calcium tungstate $CaWO_4$ heat capacity. Simon et al.[16] indicate that the ferroelastic phase transition of the second type exists at $T_C = 52$ K in calcium molybdate $CaMoO_4$. The investigations of low-temperature heat capacity of lead tungstate $PbWO_4$ samples doped with lanthanum were presented by Takai et al.[17]

In this study, experimental measurements of the molar heat capacity of wulfenite over the temperature range of (55 to 320) K have been carried out by means of vacuum adiabatic calorimetry, and the low-temperature heat capacity of the compound has been calculated using various computational approaches. On the basis of the experimental data and the smoothed values of heat capacity, the main thermodynamic functions of the mineral have been calculated.

Experimental Part

The wulfenite sample used for the research was taken from the deposit Kyzyl-Espe, Kazakhstan. The sample had well-cut tabular crystals of yellowish-orange color, about (1 to 2) mm and smaller in dimension. X-ray phase analysis has shown agreement of the sample difractogram (Figure 1) with information on wulfenite available in the crystallographic database. An infrared spectrum of the sample also demonstrated the agreement of the main absorption bands to the known experimental spectra of wulfenite. The results of electron microprobe analysis are: PbO 59.53 %, MoO_3 37.99 %, WO_3 1.71 %, CaO 0.02 %, Cr_2O_3 0.05 %, CuO 0.03 %, V_2O_5 0.09 %.

The sample heat capacity was measured in a low-temperature thermophysical unit produced by CJSC "Termis" (Moscow).

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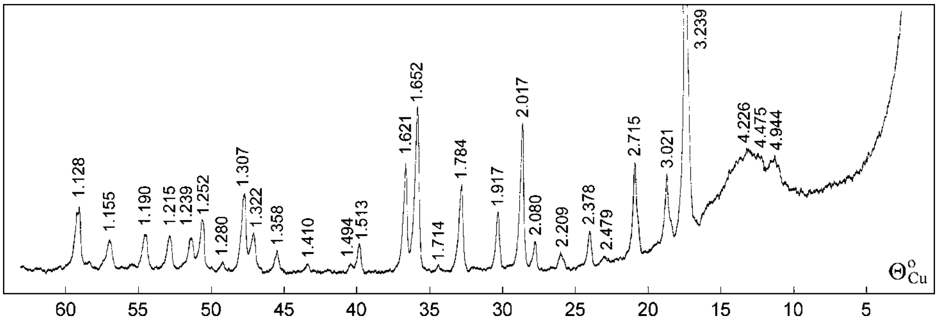

Figure 1. X-ray photograph of wulfenite.

The unit error while measuring a standard sample of the heat capacity of copper is not more than ± 1.44 % at 5 K, about ± 0.23 % at 40 K, and less than ± 0.11 % in the interval from (80 to 300) K.[18] Temperature is measured with an iron−rhodium resistance thermometer ($R_0 = 50\ \Omega$) calibrated in the VNIIFTRI in accordance with the international temperature scale ITS-90. The weight of the wulfenite sample was 1.7307 g, and measurements were carried out in a titanic container (volume 1 cm^3), which was filled with heat exchanging helium and sealed with indium foil. Heat capacity measurements were carried out starting from a temperature of 55 K, and the magnitude of a temperature stage was 2 K in the interval from (50 to 70) K and 3 K for the range (70 to 150) K. For the range (150 to 320) K a temperature stage of 1.5 K was used. The measurements resulted in 142 experimental points (Table 1). In the area from (270 to 280) K, the presence of an anomaly with a maximum at 273.4 K (Figure 2) was registered.

Discussion of the Results

A. Extrapolation of Heat Capacity to 0 K. With the aim of calculating integral thermodynamic functions (entropy, enthalpy, etc.), it is necessary to have information on heat capacity behavior in the range from (0 to 55) K. Generally, the Debye Limiting Law[19] which is true below a temperature of $\sim\Theta_D/20$ (Debye temperature)[20] is used to describe the lattice component of the heat capacity close to 0 K. In those cases, when the experimental heat capacity is known at higher temperatures (as in our case) other approximations are used. An equation to describe heat capacity of solids in a wide range of temperatures has been proposed,[21,22] which can be used while extrapolating the experimental data on heat capacity to zero

$$C(T) = (AT^{-1/\alpha\beta} + 1)^{-1/\alpha} \tag{1}$$

where α and β are dimensionless parameters which can be determined from the experiment; $C(T) = C_V/(3Rm)$; R is the universal gas constant; abd m is the number of atoms in a molar formula. Coefficient A in eq 1 is equal to

$$A = \left(\frac{4\pi^4}{5}\right)^{-\alpha} \Theta^{\alpha\beta} \tag{2}$$

where Θ is a parameter having a temperature dimension connected with the effective average frequency of phonon states density. Equation 1 has a correct asymptotic behavior both at low temperatures ($T \rightarrow 0$: $C(T) \approx A^{-1}T^{\beta}$) and at high temperatures ($T \rightarrow \infty$: $C(T) \approx 1 - 1/T^{\alpha\beta}$) for any values of α higher than zero. The low-temperature asymptotic is supported by parameter β, which reflects the structural anisotropy of the compound and can possess values from 1 to 3. Parameter α is the power with which the heat capacity approaches the limiting value of Dulong and Petit. It has been demonstrated[21,22] that there is a high accuracy in the description of the model (the Debye model, the Tarasov models) and real objects (elements, simple, and complex compounds) by means of eq 1.

Equation 1 is easily transformed to the form

$$(C^{-\alpha} - 1)^{-1/\alpha\beta} = aT \tag{3}$$

which after substitution

$$Z = (C^{-\alpha} - 1)^{-1/\alpha\beta} \tag{4}$$

takes the form of the linear homogeneous equation

$$Z = aT \tag{5}$$

where $a = A^{-1/(\alpha\beta)}$. After such a substitution, the function $Z(T)$ is a linear function of temperature. Presenting the experimental data in coordinates (eq 5), it is possible to select values of α and β so that the values $Z(T)$ lie on a straight line, and this straight line has the form of a linear homogeneous equation. The selection of the α and β values can be performed by the least-squares method.

Figure 3 shows the experimental heat capacity of $PbMoO_4$ in ordinary coordinates and in coordinates $Z-T$. The optimal parameters α and β were found by the least-squares method in the interval from (55 to 190) K and are equal to $\alpha = 0.61$ and $\beta = 1.9$.

It is evident that the dependence $Z(T)$ in the interval from (55 to 190) K is well described by the straight-line eq 5 (Figure 3, curve 4). The root-mean-square deviation of the experimental values from those obtained according to eq 5 in the interval from (55 to 190) K is 0.4 %. The value $\Theta = (655 \pm 8)$ K was found from the coefficient of approximation of the straight line. At temperatures higher than 190 K, a deviation of the experimental values from the calculated ones is observed due to reaching the limit of applicability of eq 1 at a given α and β. Data on the heat capacity below 55 K were obtained by means of extrapolation of the straight-line (eq 5) having been obtained at optimal values of α and β to 0 K. The value of parameter $\beta = 1.9$ considerably differs from the Debye index ($\beta = 3$); this fact, we suppose, is a reflection of structural anisotropy of the given compound and points out the closeness to a quasi-two-dimensional structure.

To check if parameter β had been determined correctly and evaluate the uncertainty of the $PbMoO_4$ heat capacity description by eq 1 at temperatures lower than 55 K, we analyzed the data on the heat capacity for the isostructural compound $CaWO_4$. Experimental data on the heat capacity for $CaWO_4$ were obtained by means of the adiabatic method[15] over the range

Table 1. Experimental Values of the Molar Heat Capacity of Wulfenite from T = (55.57 to 323.94) K (M = 367.1376 g·mol^{-1})

T/K	C_p/J·mol^{-1}·K^{-1}	T/K	C_p/J·mol^{-1}·K^{-1}
	Series 1		
55.57	41.511	67.85	49.945
57.87	42.875	69.85	51.260
59.86	44.414	72.35	52.821
61.86	45.970	75.38	54.630
63.85	47.349	78.41	56.467
65.85	48.726	81.45	58.301
	Series 2		
79.22	57.004	116.83	75.799
82.87	59.159	119.96	77.057
85.92	60.936	123.10	78.308
88.98	62.640	126.25	79.523
92.05	64.267	129.41	80.838
95.12	65.898	132.58	81.910
98.20	67.426	135.75	83.048
101.29	68.966	138.92	84.305
104.38	70.388	142.11	85.445
107.48	71.856	145.31	86.355
110.59	73.201	148.50	87.396
113.71	74.481	150.36	88.034
	Series 3		
146.81	86.738	236.43	108.30
150.77	88.066	238.05	108.59
153.23	88.721	239.66	108.99
154.86	89.325	241.27	109.20
156.49	89.884	242.88	109.32
158.11	90.630	244.48	109.91
159.75	90.905	246.08	110.36
161.39	91.328	247.68	110.32
163.02	91.713	249.28	111.27
164.66	92.198	250.87	111.33
166.29	92.668	252.46	111.60
167.93	93.336	254.06	112.29
169.58	93.580	255.66	112.73
171.22	93.991	257.26	113.05
172.86	94.458	258.87	113.37
174.50	94.900	260.48	113.10
176.18	95.473	262.08	114.13
177.83	95.609	263.69	114.51
179.47	95.995	265.31	114.12
181.12	96.409	266.92	115.37
182.75	97.291	268.54	115.85
184.38	97.276	270.17	116.32
186.00	97.556	271.80	116.84
187.63	97.988	273.44	118.29
189.25	98.332	275.09	117.55
190.87	98.780	276.76	117.48
192.48	99.099	278.44	117.65
194.09	99.720	280.22	116.86
195.71	99.928	281.96	117.27
197.32	100.38	283.72	117.50
198.94	100.83	285.48	117.74
200.55	101.10	287.24	118.01
202.18	101.79	289.02	118.27
203.81	101.78	290.80	118.42
205.44	102.20	292.58	118.65
207.07	102.48	294.37	118.96
208.70	102.71	296.17	119.16
210.32	103.11	297.97	119.42
211.96	103.41	299.78	119.58
213.59	103.69	301.60	119.83
215.23	104.04	301.60	119.83
216.86	104.38	303.42	120.04
218.49	104.78	305.24	120.26
220.13	104.99	307.07	120.46
221.76	105.32	309.03	119.83
223.39	105.67	310.84	120.90
225.02	106.23	312.69	121.09
226.66	106.37	314.55	121.22
228.30	106.75	316.42	121.38
229.93	107.06	318.29	121.48
231.56	107.42	320.17	121.65
233.19	107.79	322.06	121.73
234.81	108.03	323.94	121.92

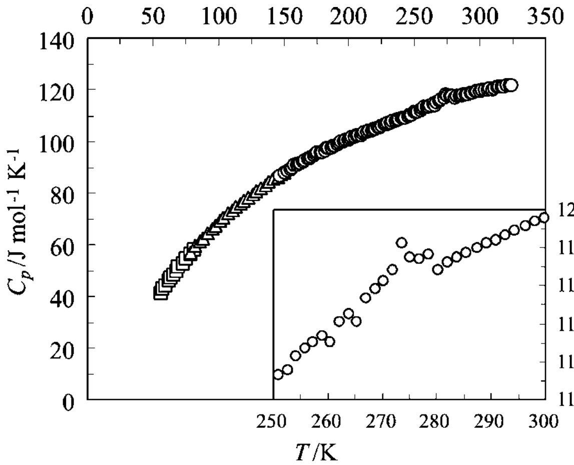

Figure 2. Temperature dependence of molar heat capacity for wulfenite $PbMoO_4$ in the range from T = (55.57 to 323.94) K. Open squares, series 1; open triangles, series 2; open circles, series 3.

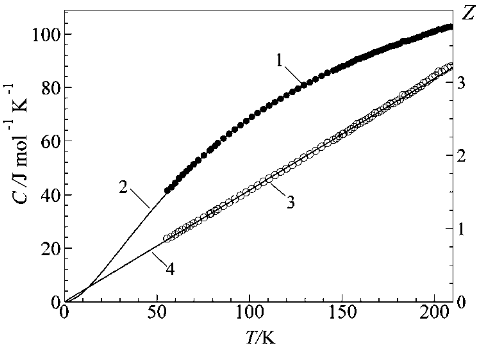

Figure 3. Heat capacity of $PbMoO_4$. Filled circles 1, experimental values of the heat capacity; curve 2, calculated regular heat capacity according to eq 1; open circles 3, lattice heat capacity in (Z,T) coordinates; straight-line 4, to obtain the optimal parameters α and β in eq 5.

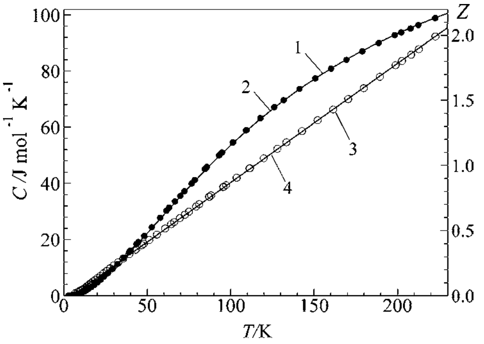

Figure 4. Heat capacity of $CaWO_4$. Filled circles 1, experimental values of the heat capacity; curve 2, calculated regular heat capacity according to eq 1; open circles 3, lattice heat capacity in (Z,T) coordinates; straight-line 4, to obtain the optimal parameters α and β in eq 5.

from (5 to 350) K. Figure 4 presents the results of description of these data by eq 5.

It is evident that in the interval from (5 to 230) K the dependence of $Z(T)$ (Figure 4, curve 3) is well described by the straight-line (eq 5) (Figure 4, curve 4). The optimal parameters obtained in this interval are $\beta = 1.9$ and $\alpha = 0.76$. It is obvious that parameter β (representing the structure features) has the same value for $CaWO_4$ and for $PbMoO_4$, justifying that this parameter for $PbMoO_4$ has been determined correctly. The mean square deviations of the experimental heat capacity values for $CaWO_4$ from those obtained according to eq 1 are: 18 % in the interval from (5 to 23) K; 1.5 % in the interval from (23 to 60)

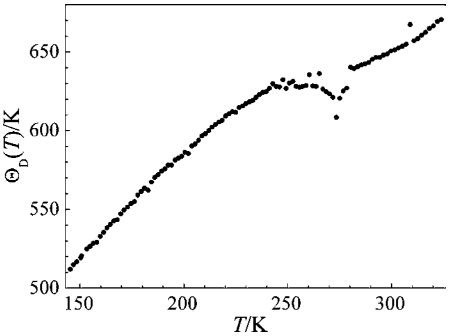

Figure 5. Behavior of the characteristic Debye temperature for wulfenite in the temperature range from (150 to 320) K.

K; and 0.6 % in the interval from (60 to 200) K. The obtained results of heat capacity description by eq 1 were used for determining the error occurring for the heat capacity extrapolation from (55 to 0) K for $PbMoO_4$.

B. Obtaining the Regular Heat Capacity in the Area of the Phase Transition. While analyzing the experimental data, an anomaly was discovered in $C_p(T)$ in the interval from (240 to 324) K, which is clearly seen on the temperature dependence of the Debye temperature $\Theta_D(T)$ (Figure 5).

To obtain information on the regular heat capacity behavior at temperatures higher than 240 K, we used the method of effective sum (MES),[23,24] which is based on high-temperature expansion of the heat capacity.

It has been shown that the molecular lattice heat capacity $C_V(T)$ in a harmonic approximation can be described by an analytical expression, the parameters of which are characteristic temperatures related to the moments of the density of phonic states $g(\omega)$[23,24]

$$\frac{C_V(T)}{3Rm} = 1 - \frac{\Theta_2^2}{12T^2} - \frac{\Theta_4^4}{\Theta_*^4} + \frac{\Theta_4^4}{T^2\Theta_*^2}\left(\frac{1}{12} + \frac{1}{\varphi(z)}\right) \qquad (6)$$

$$\varphi(z) = e^z + e^{-z} - 2, \; z = \Theta_*/T \qquad (7)$$

where R is the universal gas constant; m is the number of atoms in the formula of a substance used while determining the mass of the mole; Θ_2 and Θ_4 are characteristic temperatures related to the second and the fourth moments $g(\omega)$; and Θ_* is the characteristic temperature related to the boundary frequency of the phonon spectrum $g(\omega)$.

To determine the parameters Θ_2, Θ_4, and Θ_*, expression 6 is reduced by means of substitution of

$$X(\Theta_*, T) = \frac{1}{\Theta_*^2}\left[1 - \frac{12T^2}{\Theta_*^2} + \frac{12}{\varphi(\Theta_*/T)}\right] \qquad (8)$$

$$Y(T, C) = 12T^2\left[1 - \frac{C_V(T)}{3Rm}\right] \qquad (9)$$

to the straight-line equation

$$Y = \Theta_2^2 - \Theta_4^4 X \qquad (10)$$

As a result, the calculation is reduced to the search for the optimal value Θ_*, at which the heat capacity in the given temperature interval in coordinates $X-Y$ is best of all described by the straight-line eq 10. Parameters Θ_2 and Θ_4 are determined as coefficients of this straight-line. The optimal values Θ_2, Θ_4, and Θ_* search problem is resolved by means of a least-squares method. The details of the calculation procedure have been presented previously.[23,24]

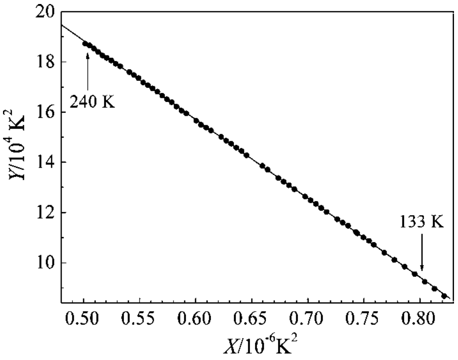

Figure 6. Result of approximation of the heat capacity for $PbMoO_4$ (filled circles) according to eq 10.

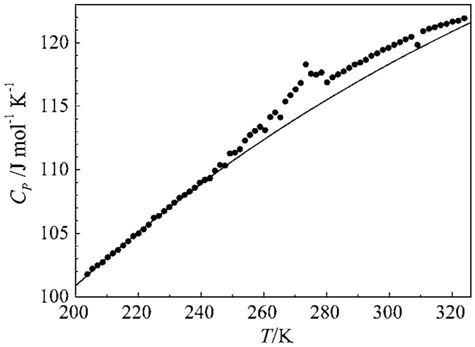

Figure 7. Behavior of experimental (filled circles) and regular (line) heat capacity of wulfenite in the temperature range from (200 to 324) K.

The expressions 6 and 10 for the heat capacity are true over a certain temperature interval: the lower boundary of this interval cannot be lower than the heat capacity point of inflection ($\sim\Theta_*/2\pi$), and it is determined by the convergence limit of the initial high-temperature expansion; the upper boundary is the temperature at which a nonlineal anharmonic contribution to the heat capacity becomes substantial. Since the dependence $\Theta_D(T)$ up to 240 K monotone grows (Figure 5) and the heat capacity at this temperature reaches 70 % of the Dulong and Petit limit value ($3Rm$), then in our case it can be assumed with a high degree of reliability that $C_p(T) \approx C_V(T)$ in the temperature interval up to 240 K.

The experimental points in coordinates $X-Y$ and the approximation straight-line 10 at the optimal parameter $\Theta_* = (1000 \pm 19)$ K are given in Figure 6.

It is seen in Figure 6 that the dependence $Y(X)$ is well described by the straight-line eq 10 in the interval from (133 to 240) K. The characteristic temperatures of the phonon spectrum $g(\omega)$, $\Theta_2 = (588 \pm 5)$ K and $\Theta_4 = (749 \pm 9)$ K, were obtained from coefficients of the straight-line (eq 10) approximation.

The confidence interval of the calculated values Θ_2, Θ_4, and Θ_* was determined according to the Fisher criterion at the level of confidence probability 0.95. The harmonic part of the heat capacity $C_V(T)$ from (200 to 325) K was calculated by means of eq 6. The mean square deviations of the experimental values from those obtained according to eq 6 in the interval from (200 to 240) K are equal to 0.16 %. Figure 7 represents the experimental and regular heat capacities in the anomaly area.

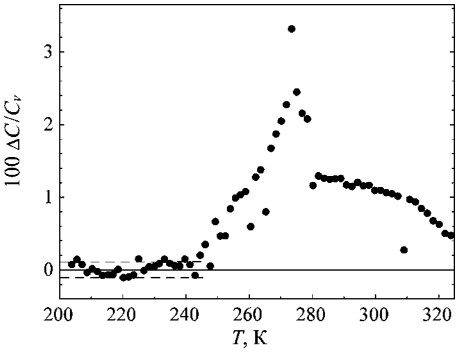

Figure 8. Relative deviations $\Delta C = C_p(\text{exp}) - C_V(\text{calc})$ of the experimental heat capacity of $PbMoO_4$ from values C_V(calc) (zero line) calculated by eq 6. Dashed lines indicate normal experimental scattering in this temperature area.

The relative deviations of the experimental values of $C_p(T)$ from the values of $C_V(T)$ obtained according to eq 6 in the interval from (200 to 325) K are given in Figure 8.

As seen from Figure 8, the deviations of the experimental values of the heat capacity from those obtained according to eq 6 do not exceed the experimental scattering in the interval from (200 to 241) K, and an anomalous increase of heat capacity reaching 3.3 % at its maximum (at $T \approx 273.4$ K) is observed in the interval from (241 to 324) K. The anomaly has the signs of a phase transition seemingly not completed at 324 K. An increased scattering of experimental points is observed on the anomaly left wing in the area from (241 to 265) K. This fact can be associated with the presence of thermal hysteresis. To clarify the nature of the phase transition, it is necessary to carry out additional investigations.

C. Calculation of Wulfenite Heat Capacity by Means of the Quantum-Chemical Method MNDO and the Method of Interatomic Potentials. The wulfenite heat capacity in the interval from (0 to 55) K has also been calculated by the semiempirical method MNDO using the program package on quantum-chemical calculation MOPAC[25] allowing calculations for crystal solids to be made. A cluster consisting of four unit cells having linear dimensions (10.8 × 10.8 × 12.1) Å was used in the calculations. The positions of atoms were assigned based on crystallographic atomic coordinates of wulfenite presented previously,[3] and they were not subject to optimization. The total number of atoms in the calculation was 96 atoms, and in this case cyclic boundary conditions were used.

At the same time, the calculation of heat capacity was carried out in the framework of crystal lattice dynamics theory through calculation of vibration states of the compound using computer program LADY.[26] Crystallographic information[3] was also used as the initial data for calculation of the compound structure. On the basis of the estimated data on the position of atoms of lead, molybdenum, and oxygen in a unit cell of the mineral, its vibration states were calculated. The estimated vibration spectra of wulfenite were reconciled with the experimental IR and Raman spectra[8−14] according to the method of interatomic potentials by means of finding parameters of interatomic interaction in the equation $u(r) = a\mathrm{e}^{-r/b}$ (where u is the potential energy, r is interatomic distance, and a and b are parameters of the interatomic potential) separately for each pair-type of atoms. A relative deviation of the vibration frequency values in the estimated spectra from the values of band positions in the experimental spectra did not exceed ± 10 %, averaging ± 5 %. After calculation of the vibration states, calculation of phonon states density and heat capacity of the compound was made.

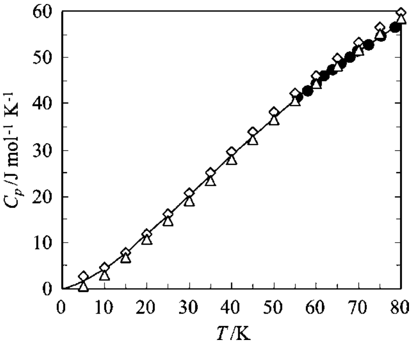

Figure 9. Experimental and calculated values of the heat capacity of $PbMoO_4$ in the helium area. Filled circles, experiment; solid curve, extrapolation by eq 1; open diamonds, MNDO calculation; open triangles, LADY calculation.

Table 2. Heat Capacity Polynomial Quotients a_n for Wulfenite from T = (55 to 320) K

	polynomial quotients			
temperature interval (K)	a_0	a_1	a_2	a_3
55 to 80	−39.755	2.4084	$-2.2071 \cdot 10^{-2}$	$8.9400 \cdot 10^{-5}$
80 to 120	−21.237	1.4529	$-7.0414 \cdot 10^{-3}$	$1.4685 \cdot 10^{-5}$
120 to 160	−28.228	1.5432	$-7.2207 \cdot 10^{-3}$	$1.3948 \cdot 10^{-5}$
160 to 210	49.436	0.1568	$1.1996 \cdot 10^{-3}$	$-3.4768 \cdot 10^{-6}$
210 to 260	16.114	0.8345	$-2.9774 \cdot 10^{-3}$	$4.6430 \cdot 10^{-6}$
260 to 273.44	−16520.32	190.850	$-7.3071 \cdot 10^{-1}$	$9.3361 \cdot 10^{-4}$
273.44 to 290	21482.12	−223.467	$7.7862 \cdot 10^{-1}$	$-9.0370 \cdot 10^{-4}$
290 to 320	696.43	−6.2166	$2.1805 \cdot 10^{-2}$	$-2.4973 \cdot 10^{-5}$

The estimated data on wulfenite heat capacity obtained by means of the different methods are given in Figure 9.

The heat capacity values calculated by the MNDO method are somewhat overestimated for temperatures lower than 10 K due to restrictions and assumptions existing in MOPAC. The values calculated in LADY agree nicely with the experimental data due to the agreement of spectra. These values are phonon contribution into the total heat capacity of the compound proportional at low temperatures T^3; therefore, they are slightly underestimated in comparison with the values estimated according to eq 1 below 15 K. By and large, the estimated values of wulfenite heat capacity for temperatures lower than 55 K obtained by different methods agree nicely with themselves and the experimental data.

D. Calculation of Thermodynamic Functions of Wulfenite. For a mathematical description of the temperature dependence of the wulfenite heat capacity, we used a spline-approximation of the experimental values by a third power polynomial. No fewer than 3 to 4 points overlapped the experimental points in the areas of the change of polynomials. The values of coefficients of the heat capacity fitting polynomials in the corresponding temperature intervals are given in Table 2.

The root-mean-square deviation of experimental points from fitting curves did not exceed ± 0.49 % at (55 to 60) K, ± 0.05 % at (60 to 140) K, ± 0.11 % at (140 to 240) K, ± 0.23 % at (240 to 280) K (in the area of the phase transition), or ± 0.07 % at (280 to 325) K. The relative deviation of experimental points from the smoothed values is given in Figure 10.

On the basis of the coefficients found for the heat capacity polynomials, the tabulated values of wulfenite thermodynamic functions have been found. They are given in Table 3.

The errors of thermodynamic values given in the table took shape from the unit errors while measuring the standard sample of heat capacity measured in the interval from (55 to 320) K

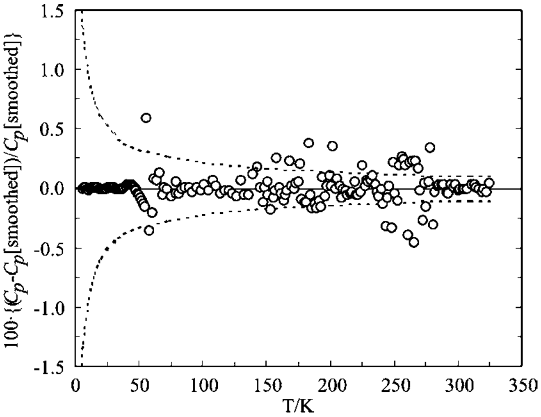

Figure 10. Percentage deviations of experimental values of wulfenite heat capacity from the fitting polynomials. Dotted lines indicate 95 % range of uncertainty of calorimetric unit.

Table 3. Molar Thermodynamic Functions of Wulfenite from T = (5 to 320) K (M = 367.1376 g·mol^{-1})

T	$C_{p,\mathrm{m}}$	$\Delta_0^T S_\mathrm{m}^\circ$	$\Delta_0^T H_\mathrm{m}^\circ / T$	Φ_m°
K	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-1}	J·mol^{-1}·K^{-1}
5	1.69	1.57	0.797	0.774
10	4.38	3.52	1.88	1.64
15	7.82	5.93	3.27	2.66
20	11.74	8.70	4.89	3.81
25	15.91	11.77	6.67	5.09
30	20.19	15.05	8.57	6.48
35	24.49	18.48	10.54	7.95
40	28.72	22.03	12.55	9.48
45	32.85	25.65	14.57	11.08
50	36.88	29.32	16.60	12.72
55	40.78	33.02	18.63	14.40
60	44.60	36.74	20.64	16.10
65	48.09	40.45	22.61	17.83
70	51.35	44.13	24.55	19.58
75	54.44	47.78	26.44	21.34
80	57.44	51.39	28.29	23.10
85	60.40	54.96	30.09	24.87
90	63.19	58.50	31.85	26.64
95	65.83	61.98	33.57	28.41
100	68.32	65.42	35.25	30.18
110	72.93	72.16	38.47	33.69
120	77.09	78.68	41.51	37.17
130	81.01	85.01	44.40	40.61
140	84.57	91.15	47.15	44.00
150	87.87	97.09	49.75	47.34
160	90.97	102.9	52.23	50.63
170	93.67	108.5	54.59	53.87
180	96.24	113.9	56.84	57.05
190	98.68	119.2	58.97	60.18
200	101.0	124.3	61.02	63.26
210	103.1	129.3	62.97	66.29
220	105.0	134.1	64.84	69.26
230	107.0	138.8	66.63	72.18
240	109.1	143.4	68.35	75.05
250	111.2	147.9	70.02	77.88
260	113.4	152.3	71.65	80.66
270	116.3	156.6	73.24	83.39
273.15	117.9	158.0	73.75	84.24
280	117.2	160.9	74.82	86.08
290	118.4	165.0	76.30	88.73
298.15	**119.4 ± 0.1**	**168.3 ± 2.1**	**77.46 ± 0.17**	**90.86 ± 3.74**
300	119.6	169.1	77.72	91.34
310	120.8	173.0	79.09	93.92
320	121.6	176.9	80.41	96.45

and the error of experimental data extrapolation to absolute zero for temperatures below 55 K.

Conclusion

The calculated standard values of the thermodynamic functions of wulfenite satisfactorily agree with the values given in the references 2 and 3. This fact verifies the correctness of the heat capacity extrapolated values calculation according to eq 1 over the range of (0 to 55) K.

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