

Low-Temperature Thermal Properties of Calcium Tungstate*

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(Received 24 June 1968)

The heat capacity of a single crystal of CaWO_4 was determined by adiabatic calorimetry from 5° to 350°K and found to be without transitions or thermal anomalies. Deviation of the curve from normal sigmoid shape is shown to be due to internal vibrations of the WO_4^{2-} ions. Apparent Debye θ 's for the lattice-only heat capacity and for that of the acoustical spectrum show "normal" deviation from simple Debye theory. Values of the heat capacity (C_p), entropy (S°), enthalpy function $[(H^\circ - H_0^\circ)/T]$, and Gibbs function $[(G^\circ/H_0^\circ)/T]$ at 298.15°K are 27.28, 30.21, 16.02, and -14.19, in calories per gram formula mass-degree Kelvin.

I. INTRODUCTION

Scheelite-type crystal structures are currently of great interest in laser technology as hosts for lanthanide ions.¹⁻³ Calcium tungstate is particularly useful for the study of the properties of impurities and defects in these crystals.¹ Of fundamental importance in further development of the technology of materials of this type is an understanding of the lattice and molecular vibrations associated with this relatively complex structure.^{4,5} In reporting their paramagnetic relaxation measurements on Ce, Nd, and Yb in CaWO_4 , Kiel and Mims⁴ noted that the observed T^{11} dependence could only be explained by assuming a Debye temperature of about 140°K. For this reason the present investigation was undertaken on single-crystal CaWO_4 of high purity to provide experimental verification and a significant extension to lower temperatures of the thermal studies on CaWO_4 by King and Weller.⁵

II. EXPERIMENTAL

A. Cryogenic Apparatus

Measurements were made in the Mark II adiabatic cryostat previously described.⁷ The gold-plated, copper calorimeter of about 23 cm³ capacity (laboratory designation W-49) with an off-axis thermometer-heater-well, was employed for measurements on the sample. Temperatures determined with a capsule-type, platinum-resistance thermometer (laboratory designation A-5)

are considered to be in accord with the thermodynamic temperature scale within 0.03°K from 10°-90°K and within 0.04°K from 90°-350°K. The heat capacity of the empty calorimeter was determined separately with appropriate small corrections for the slight differences in the amounts of helium, indium-tin solder, and Apiezon-T grease on the loaded and on the empty calorimeter. The heat capacity of the 45.559-g sample represented about 44% of the total at 15°K and gradually increased to 73% near 300°K. The buoyancy correction was made on the basis of a sample density of 6.12 g/cm³.⁸ Helium gas (about 28 torr at 300°K) was used to enhance thermal contact between calorimeter and sample. All determinations of mass, voltage, current, and temperature were referred to calibrations performed by the National Bureau of Standards.

B. Preparation and Purity of Sample

The single crystal of CaWO_4 was prepared by R. T. Farrar of the Harry Diamond Laboratory from Sylvania crystal-grade powder by the Czochralski method. The typical manufacturer's analysis of the powder supplied indicated the following (in parts per million): Al, 50; Ba, 50; Mg, 50; Si, 50; Sr, 100; Fe, 5; Mo, 5; Na, 5. Electron spin resonance measurements by D. R. Mason of the Nuclear Engineering Department of the University revealed the presence of the additional impurities: Mn, V, Nb, and Ta in concentrations of a few parts per million.

III. RESULTS AND DISCUSSION

A. Heat Capacities and Thermal Properties

The experimental heat-capacity values for CaWO_4 are presented in Table I in chronological sequence at the mean temperatures of the determinations. Hence temperature increments employed in the measurements may usually be inferred from the differences in the adjacent mean temperatures. These data have been adjusted for

* Supported by the Division of Research of the U.S. Atomic Energy Commission.

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² L. N. Bykhovskaya, I. M. Gurevich, S. V. Kononova, I. S. Neiman, and F. A. Charnaya, *Zh. Prikl. Spektrosk.* **7**, 12 (1967).

³ A. A. Antipin, A. N. Katyshev, I. N. Kurkin, and L. Ya. Shekun, *Fiz. Tverd. Tela* **9**, 813 (1967) [*Sov. Phys.—Solid State* **9**, 630 (1967)].

⁴ A. Kiel and W. B. Mims, *Phys. Rev.* **161**, 386 (1967).

⁵ M. I. Kay, B. C. Frazer, and I. Almodovar, *J. Chem. Phys.* **40**, 504 (1964).

⁶ E. G. King and W. W. Weller, *U. S. Bur. Mines Rept. Invest.* 5791 (1961).

⁷ E. F. Westrum, Jr., *J. Chem. Educ.* **39**, 443 (1962).

⁸ R. D. Shapovalova, N. P. Mikhailova, and Ya. J. Gerasimov, *Russ. J. Phys. Chem. (English Transl.)* **34**, 978 (1960).

"curvature" occasioned by the finite temperature increments employed in the measurements and are considered to have a probable error decreasing from about 3% at 5°K to 0.5% at 10°K and to less than 0.1% above 20°K. These data are based upon a defined thermochemical calorie equal to 4.1840 J, an ice point of 273.15°K, and a gram formula mass of 287.928.

The smoothed heat capacities and thermodynamic functions at selected temperatures obtained by integrating these data with a high-speed digital computer are given in Table II. The heat-capacity values of Table II were taken from a smooth curve obtained by a least-squares-fitted polynomial function through the experimental points. The thermodynamic functions are

TABLE I. Heat capacity of calcium tungstate.*

<i>T</i>	<i>C_p</i>	<i>T</i>	<i>C_p</i>
Series I		Series V	
64.33	7.228	95.77	12.004
69.45	8.026	103.65	13.049
74.98	8.882	111.58	14.078
81.12	9.850	119.80	15.101
88.26	10.964	127.96	16.039
97.19	12.194		
Series II		Series VI	
133.42	16.64	6.73	0.019
142.76	17.61	8.34	0.041
152.08	18.49	9.40	0.068
161.41	19.32	10.49	0.099
170.43	20.07	11.63	0.128
179.77	20.79	12.80	0.166
189.45	21.50	13.99	0.246
198.88	22.17	15.14	0.332
208.11	22.73	16.25	0.397
		17.44	0.496
		18.74	0.615
		20.24	0.754
		21.92	0.930
		23.74	1.139
		25.69	1.372
		27.70	1.624
		29.95	1.916
		32.59	2.278
		35.59	2.703
		39.23	3.232
		43.35	3.848
		47.86	4.565
		Series VII	
		Δ <i>H</i> Detn B	
		42.44	3.710
		46.81	4.387
		51.30	5.094
		55.85	5.823
		60.73	6.620
		66.07	7.488
		72.57	8.487
		79.22	9.548
		87.01	10.777
		95.40	11.947
		103.52	13.041
		111.21	14.064
		Series VIII	
		Δ <i>H</i> Detn A	
202.73	22.40		
212.76	23.02		
222.71	23.63		
231.70	24.12		
240.89	24.64		
250.28	25.11		
259.54	25.56		
268.66	26.00		
277.65	26.42		
286.85	26.83		
296.25	27.19		
305.52	27.57		
314.67	27.96		
		Series IX	
		Δ <i>H</i> Detn A	
304.54	27.48		
313.74	27.85		
322.83	28.16		
331.83	28.49		
339.85	28.76		
346.93	29.02		
		Series X	
		Δ <i>H</i> Detn A	
87.18	10.793		

* Units: calorie, gram formula mass, degree Kelvin.

TABLE II. Thermodynamic functions for calcium tungstate.*

<i>T</i>	<i>C_p</i>	<i>S°</i>	<i>H° - H₀°</i>	$-(G° - H_0°)/T$
5	0.010	0.003	0.01	0.001
10	0.078	0.024	0.18	0.006
15	0.310	0.093	1.07	0.022
20	0.732	0.236	3.60	0.056
25	1.288	0.457	8.61	0.113
30	1.924	0.747	16.61	0.194
35	2.616	1.095	27.94	0.297
40	3.348	1.492	42.84	0.421
45	4.106	1.930	61.46	0.564
50	4.892	2.403	83.94	0.724
60	6.501	3.437	140.89	1.088
70	8.113	4.560	214.0	1.503
80	9.684	5.747	303.0	1.959
90	11.181	6.974	407.4	2.448
100	12.587	8.226	526.3	2.963
110	13.899	9.488	658.8	3.499
120	15.121	10.750	804.0	4.050
130	16.26	12.006	961.0	4.614
140	17.32	13.250	1128.9	5.187
150	18.30	14.479	1307.0	5.765
160	19.20	15.69	1495	6.348
170	20.04	16.88	1691	6.932
180	20.82	18.05	1895	7.518
190	21.54	19.19	2107	8.102
200	22.22	20.31	2326	8.685
210	22.86	21.41	2551	9.265
220	23.46	22.49	2783	9.842
230	24.04	23.55	3021	10.415
240	24.58	24.58	3264	10.983
250	25.10	25.60	3512	11.548
260	25.59	26.59	3766	12.107
270	26.07	27.56	4024	12.662
280	26.52	28.52	4287	13.211
290	26.95	29.46	4554	13.755
300	27.35	30.38	4826	14.294
350	29.14	34.73	6238	16.908
273.15	26.21	27.87	4106	12.84
298.15	27.28	30.21	4775	14.19

* Units: calorie, gram formula mass, degree Kelvin.

considered to have a precision corresponding to a probable error of less than 0.1% above 100°K. An additional digit beyond those significant is given in Table II for internal consistency and to permit interpolation and differentiation. The entropies and Gibbs energies have not been adjusted for nuclear-spin and isotopic-mixing contributions, and are hence practical values for use in chemical thermodynamic calculations. In Fig. 1, the heat-capacity curves are plotted for CaWO₄, both from this research and from the work of King and Weller.⁶ Agreement over the common region of investigation is well within the limits of uncertainty given by the latter authors.

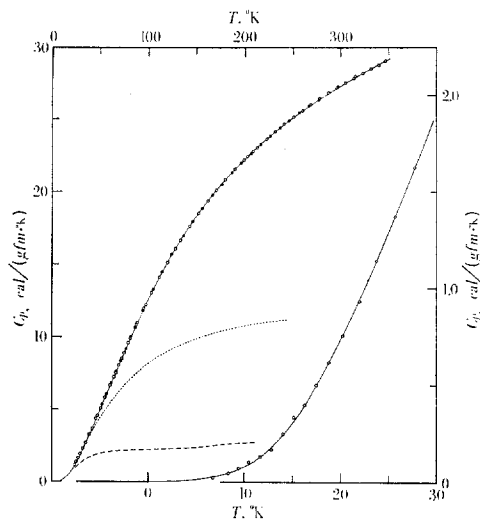


FIG. 1. Experimental heat capacity for CaWO_4 : this research, \circ —; King and Weller⁸, \bullet —; lattice-only heat contribution, \cdots ; and acoustical contribution, $---$.

High-temperature enthalpy determinations on CaWO_4 have been reported by Yakovleva and Rezukhina.⁹ The heat-capacity equation derived from their investigation is

$$C_p = 26.48 + 10.945 \times 10^{-3}T$$

in calories per gram formula mass·degree Kelvin. This equation yields $C_p = 29.74$ cal/gfm·°K at $T = 298.15^\circ\text{K}$.

As seen from Fig. 1, the experimental heat capacity for CaWO_4 deviates considerably from normal sigmoidal shape. The recent infrared,¹⁰ Raman,^{11,12} and theoretical¹³ investigations of single-crystal CaWO_4 suggest that to a good approximation, vibrational modes in the crystal correlating with modes in WO_4^{2-} ions in aqueous solution (with T_d symmetry) may be considered to be internal to the crystalline ion (with D_{2d} symmetry). Hence, appropriate Einstein contributions for each of the 18 modes assigned by Scott¹³ to the crystalline WO_4^{2-} ion were subtracted from the experimental C_p curve. The resulting curve, which approximates the heat capacity due to lattice-only vibrations is also given in Fig. 1. This curve shows the normal sigmoidal shape and $6R$ limiting value of C_p , typical of a diatomic, ionic solid. The temperature dependence of the effective θ_D calculated from this "diatomic" lattice-only C_p (per gram-atom) is shown in Fig. 2, and has a shape similar to

θ_D -vs- T curves for diatomic solids such as the alkali halides.¹⁴

B. Optical Branch Frequencies and Acoustical Spectrum

Since the optical lattice modes are known from the work of Barker¹⁰ and Porto and Scott,¹² additional Einstein contributions for these modes were subtracted from the lattice-only C_p to yield an approximation to the heat capacity associated with the acoustical modes. This curve also shown in Fig. 1 has normal sigmoidal shape with a limiting C_p near $\frac{3}{2}R$. The $\theta_D(T)$ calculated from this acoustical C_p is given in Fig. 2. The limiting value of θ_D at 0°K (θ_0) appears to be near 150°K but may be uncertain by nearly 10°K in view of the multiple approximations involved. It is apparent that C_p values in the region below 4°K are desiderata for accurate evaluation of this parameter. However, this value of θ_0 does appear to be in reasonable agreement with the value $\theta_D = 140^\circ\text{K}$ assumed by Kiel and Mims⁴ to explain low-temperature paramagnetic relaxation measurements on doped CaWO_4 . The elastic constant data of Gerlich¹⁵ are unfortunately too incomplete to permit an accurate estimate of θ_0 , but are not inconsistent with the above results. The room-temperature elastic constant data of Alton and Barlow¹⁶ on (isostructural) CaMoO_4 yields a Debye θ value of 191°K by the method of Anderson.¹⁷ In this calculation, the total number of acoustical degrees of freedom per formula unit was taken as $\frac{3}{2}$, in accordance with the group-theoretic vibrational analysis given by Barker.¹⁰ A calculation of the acoustical θ_D , similar to that carried out for CaWO_4 , using the CaMoO_4 frequency assignments of Barker, of Porto and Scott,¹² and of Scott¹³ and the incomplete CaMoO_4 heat-capacity

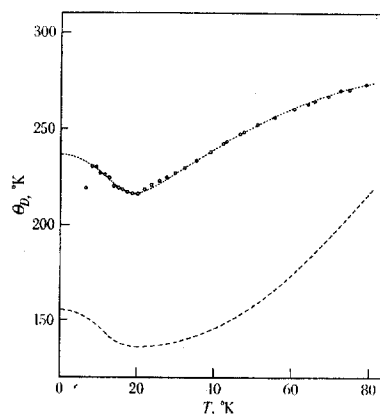


FIG. 2. Apparent Debye characteristic temperatures for CaWO_4 . Lattice-only heat capacity, \bullet —; acoustical heat capacity, $---$.

⁹ R. A. Yakovleva and T. N. Rezukhina, *Zh. Fiz. Khim.* **34**, 819 (1960) [*Russ. J. Phys. Chem. (English Transl.)* **34**, 978 (1960)].

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¹⁴ W. T. Berg and J. A. Morrison, *Proc. Roy. Soc. (London)* **A242**, 467 (1957).

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¹⁷ O. L. Anderson, *J. Phys. Chem. Solids* **24**, 909 (1963).

data of Weller and King¹⁸ yields a value near 50°K (about 174°K) which is about 8% higher than the corresponding value at this temperature for CaWO₄.

Note added in proof: Dr. Bernard Yates of the University of Salford, U.K., has informed us that he has recently measured the low-temperature heat capacity, thermal expansion, and compressibilities of CaWO₄. These data should permit evaluation of C_v and

¹⁸ W. W. Weller and E. G. King, U.S. Bur. Mines Rept. Invest. 6147 (1963).

θ_D values and hence facilitate correlations at higher temperatures.

ACKNOWLEDGMENTS

The authors thank Dr. David R. Mason and Professor Chihiro Kikuchi for their interest and for the loan of the single crystal grown by R. T. Farrar, as well as Mrs. Soung-Sik Kim for assistance in making the measurements and J. T. S. Andrews for making available certain digital computer programs.

Perturbation Theory and the Equation of State of Mixtures of Hard Spheres*

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(Received 13 May 1968)

The equation of state of a mixture of hard spheres of diameter σ_{11} and σ_{22} is evaluated by expanding the free energy of the mixture to second order in powers of the differences $\sigma_{\alpha\beta} - \sigma$, where $\sigma_{\alpha\beta} = \frac{1}{2}(\sigma_{\alpha\alpha} + \sigma_{\beta\beta})$ and σ is the diameter of the unperturbed hard spheres. The parameter σ is chosen to make the sum of the first-order terms zero. The second-order terms are evaluated using the superposition approximation, and the equation of state is determined by analytic differentiation. The agreement of this perturbation calculation with quasiexperimental Monte Carlo and molecular dynamics results is excellent, even for quite large values of $R = \sigma_{22}/\sigma_{11}$, but becomes less satisfactory as R becomes very large.

I. INTRODUCTION

Recently, we have formulated¹⁻³ a successful perturbation theory of single-component fluids. In this approach the attractive potential is treated as a perturbation on the hard-sphere potential, where the hard-sphere diameter is chosen to take into account the softness of the repulsive potential.

Currently, we are applying perturbation theory to the theory of fluid mixtures. The simplest fluid mixture is a mixture of hard spheres. In this article we use perturbation theory to calculate the equation of state of this system. Comparison of our results with quasiexperimental molecular dynamics⁴ and Monte Carlo^{5,6} calculations shows that our perturbation theory converges rapidly and yields excellent results, even when the ratio R of the diameters of the hard spheres is quite

large. However, as R becomes very large the convergence becomes slower and the results become less satisfactory.

II. FIRST-ORDER PERTURBATION THEORY

We consider a system of N_1 hard spheres of diameter σ_{11} (species 1) and N_2 hard spheres of diameter $\sigma_{22} = R\sigma_{11}$ (species 2) occupying a volume V . The potential energy of this system consists of a sum of intermolecular potentials,

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i < j} u(\alpha_i, \alpha_j; r_{ij}), \quad (1)$$

where $\alpha_i = 1$ or 2 if molecule i is of species 1 or 2,

$$u(\alpha, \beta; r_{ij}) = +\infty, \quad r_{ij} < \sigma_{\alpha\beta}, \\ = 0, \quad r_{ij} > \sigma_{\alpha\beta}, \quad (2)$$

and

$$\sigma_{\alpha\beta} = \frac{1}{2}(\sigma_{\alpha\alpha} + \sigma_{\beta\beta}). \quad (3)$$

The free energy F of the hard-sphere mixture is given by

$$F = -kT \ln \int \exp\left(-\frac{U}{kT}\right) d\mathbf{r}_1 \dots d\mathbf{r}_N$$

$$+\text{terms independent of } V \text{ and the } \sigma_{\alpha\beta}. \quad (4)$$

We now expand F in a Taylor series in $(\sigma_{\alpha\beta} - \sigma)$, where σ is the sphere diameter in the unperturbed one-com-

* This research has been supported by grants from the U.S. Department of the Interior, Office of Saline Water, and the National Research Council of Canada.

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