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Low temperature thermal properties of cobalt(II) bromate hexahydrate[1]

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Abstract

The heat capacity of cobalt(II) bromate hexahydrate $Co(H_2O)_6(BrO_3)_2$ was measured at temperatures between 13 and 310 K. Infrared and Raman spectra of the crystal were recorded in the frequency range of 400–4000 cm^{-1} for the former and 50–4000 cm^{-1} for the latter. The heat capacity data were analyzed in harmonic approximation using Debye and Einstein heat capacity functions. Some of the characteristic frequencies of the heat capacity functions were taken from the vibrational spectra and others determined by non-linear least squares fitting of the heat capacity function to the experimental heat capacity data. One Debye temperature (92 ± 1 K) and three Einstein temperatures (123 ± 2 K, 231 ± 1 K, 614 ± 50 K) were determined as functions of the temperature interval of the heat capacity data used for the fitting. The best-fit characteristic temperatures were constant, except for the third Einstein temperature, against variation of the upper limit temperature of the fitting interval from 16 to 280 K with the lower limit temperature being kept at 13 K. The Debye temperature agreed with a value of 92.4 K derived from the sound velocity. The best-fit Einstein temperatures have counterparts in the Raman spectrum in the lattice vibration region. This is the first detailed analysis of heat capacity data on a structurally complex crystal in which acoustic phonon frequencies from thermal and elastic properties are favorably compared.

Keywords: Cobalt(II) bromate hexahydrate; Heat capacity; Debye temperature; Einstein temperature; IR spectrum; Raman spectrum

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1. Introduction

The Einstein [1] and Debye [2] theories of harmonic solids have been successfully used in qualitative discussion of thermophysical properties of solids involving phonons and phonon interactions as well as in quantitative representation of thermodynamic properties of solids. It is now established that thermal properties of a solid can be calculated accurately, within the harmonic approximation, once the distribution function of the normal mode frequencies is known [3].

The frequency distribution function is represented well by the Debye ω^2 law in the low frequency limit, while the functional form is more complicated at higher frequencies with various types of van Hove singularities and gaps occurring at different frequencies. The lattice spectrum, i.e. the frequency distribution function, may be calculated by the lattice dynamics of Born and von Karman [4,5] who showed how to determine the normal mode frequencies of a crystal lattice from the equation of motion of the atoms forming the crystal. Thus, the heat capacity of a crystal can be calculated, in principle, from the knowledge of intra- and intermolecular forces. Also in practice, a lattice dynamical calculation produces realistic phonon spectra for simple crystals. They can be compared with neutron scattering and calorimetric experiments [6]. Although this frame work of lattice dynamics, statistical mechanics and thermodynamics has been well established, actual calculation of the heat capacity of a solid involves a large number of parameters whose values are not known. It is obviously desirable to develop transferable interatomic potentials or even methods for accurate ab initio lattice dynamical calculation.

From the experimental point of view, we are often interested in anomalous heat capacities such as those due to phase transitions and want to separate them from the vibrational heat capacity. For such purposes, the original Debye and Einstein theories are easy to use and give apparently reasonable results, and have actually been employed in many cases [7–25] assuming that these theories are applicable to more complex crystals as well. The same theories have been extended to deal with thermal expansion of solids [26]. It was, therefore, desirable to test the consistency of such calculations for substances considerably more complex than metals and alkali halides.

In the present paper, we describe the analysis of the heat capacity of a fairly complex coordination compound by the use of the Einstein and Debye theories, and compare the result with elastic and expansivity data.

Cobalt(II) bromate hexahydrate $Co(H_2O)_6(BrO_3)_2$ crystallizes in a cubic structure [27]. In this crystal, all the cobalt atoms are equivalent and so are all the water molecules and bromate ions [28,29]. We chose this compound for our investigation because of this structural regularity in contradistinction to its complex chemical composition. Because of the cubic symmetry, the number of independent elastic constants is small, which makes the analysis of the relation between the mechanical and thermal properties simpler than otherwise. It is important that a complete set of the elastic constants and the thermal expansivity has been measured [30]. The high symmetry of the crystal is intrinsic rather than an averaged property; all the atoms including hydrogen atoms are ordered. This was confirmed by the absence of any anomaly in the heat capacity.

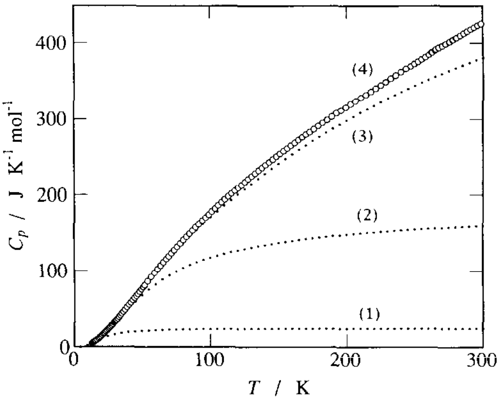

Fig. 1. Molar heat capacities of $Co(H_2O)_6(BrO_3)_2$. The curves represent calculated heat capacities. (1) Debye term, optimized; (2) Debye and Einstein terms, optimized; (3) calculated vibrational heat capacities at constant volume; (4) experimental molar heat capacities, open circles. Calculated heat capacities at constant pressure agree with the experimental values well within the size of the circles representing the latter.

2. Experiment and its result

Barium bromate was prepared from barium chloride and potassium bromate. Its reaction with cobalt(II) sulfate gave an aqueous solution of cobalt(II) bromate and insoluble barium sulfate. Cobalt(II) bromate hexahydrate was obtained from the filtered solution by evaporation of the water [28]. The air-dried crystal, pink-red in color, was stable when kept in ambient atmosphere: 6.2429 g (in vacuo) of the crystals, 1–3 mm at the edges were sealed in a gold plated copper sample cell of a computer controlled adiabatic calorimeter [31,32]. The heat capacity was measured at 13 K intervals between 13 and 310 K.

The heat capacity varied smoothly with temperature as Fig. 1 shows, following the general course of the temperature dependence of the vibrational heat capacity. At 268.2 K, a slight deviation from the normal behavior occurred. It was due to melting of a small amount of ice formed from occluded aqueous solution of recrystallization. The peak did not occur in a run in which the sample had been cooled to 250 K, because the occluded solution supercooled in this series. The amount of the occluded aqueous solution was 4.9 mg in 6.2429 g of the sample as estimated from the enthalpy of fusion of the ice. The impurity was corrected for in the calculation of the molar heat capacities given in Table 1.

The infrared absorption spectrum was recorded with a Fourier transform JASCO FT/IR3 spectrometer on a powdered sample dispersed in paraffin. The sample was guarded against dehydration by a pair of KBr plates sandwiching the mulled sample. The Raman spectra were recorded with a JASCO R800 spectrometer using a helium-neon laser source. The infrared and Raman spectra are reproduced in Figs. 2 and 3. The peaks were assigned tentatively by comparison with published data [33–37]. Wave numbers of the peaks are given in Table 2.

Table 1

Experimental molar heat capacities of $Co(H_2O)_6(BrO_3)_2$.

T/K	C_p/ J K^{-1} mol^{-1}	T/K	C_p/ J K^{-1} mol^{-1}	T/K	C_p/ J K^{-1} mol^{-1}	T/K	C_p/J K^{-1}
13.26	5.271	49.36	76.06	127.69	220.9	239.61	362.2
13.97	6.017	50.60	78.96	130.23	224.7	243.44	366.6
14.60	6.752	50.71	79.30	132.76	228.5	247.00	369.7
15.29	7.591	51.80	81.61	135.31	232.2	249.71	372.8
16.08	8.622	53.94	86.74	137.90	235.8	252.41	375.7
17.01	9.890	56.56	92.39	140.48	239.5	255.09	378.7
18.06	11.41	59.02	97.57	143.08	243.2	257.76	381.8
19.03	12.89	61.35	102.5	145.72	247.0	260.42	385.0
19.94	14.36	63.56	107.2	148.35	250.6	262.42	388.1
20.85	15.86	65.67	111.6	151.01	254.2	263.06	388.0
21.78	17.43	67.70	115.9	153.70	258.1	265.04	390.8
22.66	18.94	69.65	119.8	156.37	261.4	265.68	391.8
23.55	20.53	71.54	123.8	159.08	265.0	267.64	393.6
24.43	22.15	73.59	127.8	161.82	268.7	270.23	396.4
25.27	23.72	75.81	132.2	164.54	272.4	272.81	399.0
26.11	25.30	78.06	136.6	167.30	276.2	275.37	401.6
26.95	26.89	80.34	141.2	170.08	279.7	275.86	402.1
27.81	28.61	82.58	145.3	172.85	283.0	277.93	404.1
28.69	30.22	84.84	149.5	175.88	286.9	278.42	404.7
29.50	32.33	87.14	153.7	179.18	291.2	280.47	406.8
30.26	33.91	89.40	158.1	182.46	295.2	280.96	407.3
31.05	35.36	91.69	162.2	185.80	299.1	283.50	410.0
31.87	37.03	94.02	166.3	189.20	303.5	286.02	412.7
32.76	39.01	96.31	170.4	192.58	307.8	288.54	415.4
33.77	41.22	98.64	174.3	196.02	311.5	291.04	418.2
34.88	43.60	101.00	178.5	199.51	315.7	293.53	420.6
36.04	46.12	103.34	182.5	202.99	319.9	296.00	423.2
37.32	48.97	105.70	186.5	206.52	323.9	298.47	425.5
38.76	52.13	108.11	190.6	210.10	328.1	300.93	428.2
40.18	55.28	110.48	194.5	213.67	332.1	303.37	431.0
41.57	58.39	112.90	198.3	217.29	336.3	305.81	433.2
42.95	61.46	115.34	201.8	220.97	340.6	308.23	435.7
44.26	64.44	117.77	205.7	224.62	344.8	310.64	438.5
45.57	67.37	120.22	209.5	228.33	349.4		
46.86	70.32	122.72	213.3	232.08	353.9		
48.11	73.22	125.19	217.2	235.82	357.9		

3. Discussion

The absence of anomalies in the heat capacity curve suggests that it may be reproduced by a collection of harmonic oscillator contributions. In the following we show that this is actually the case. We utilize the spectroscopic data to determine Einstein temperatures of the intramolecular vibrations, assuming that normal modes of neighboring molecules are independent of each other.

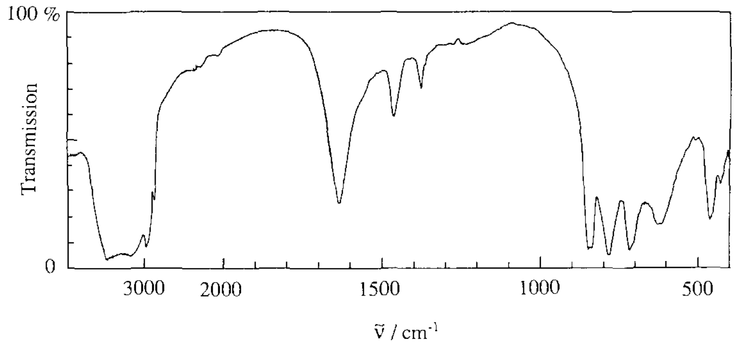

Fig. 2. Infrared spectrum of $Co(H_2O)_6(BrO_3)_2$.

3.1. Model heat capacity function

The model heat capacity function consisted of three parts; C(1) the heat capacity due to intramolecular vibrations whose frequencies can be found in the spectroscopic data, C(2) the heat capacity due to lattice vibrations whose characteristic temperatures are determined by comparison with the heat capacity data, and (3) small correction terms for the difference between C_p and C_v and for an electronic excitation of the cobalt(II) ion.

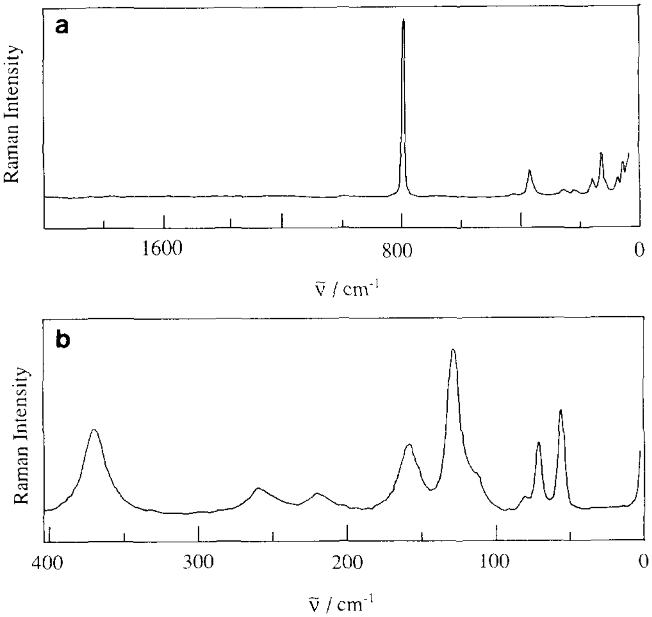

Fig. 3. (a) Raman spectrum of $Co(H_2O)_6(BrO_3)_2$. 0–2000 cm^{-1} region. (b) Raman spectrum of $Co(H_2O)_6(BrO_3)_2$, 0–400 cm^{-1} region.

Table 2

Wave numbers of the IR and Raman peaks of $Co(H_2O)_6(BrO_3)_2$

ν/cm^{-1}		Assignment	Ref.
IR	Raman		
3275		H_2O ν_1, ν_3	[35]
1634		H_2O ν_2	[35]
848		H_2O rock.	[37]
838			
784	797.8	BrO_3^- ν_1	[36]
717		BrO_3^- ν_3	[36]
627		H_2O wag.	[37]
617			
462		BrO_3^- ν_2	[36]
	427.5	$Co(H_2O)_6^{2+}$ ν_6	[32–34]
	368.1	BrO_3^- ν_4	[35]
		$Co(H_2O)_6^{2+}$ ν_1	[32–34]
	259.9	$Co(H_2O)_6^{2+}$ ν_3	[32–34]
	254.4	$Co(H_2O)_6^{2+}$ ν_5	[32–34]
	220.6	$Co(H_2O)_6^{2+}$ ν_2	[32–34]
	159.5	$Co(H_2O)_6^{2+}$ ν_4	[32–34]
	132.0	Lattice vibration	
	110	l.v.	
	79	l.v.	
	71	l.v.	
	55	l.v.	

For calculation of C(1), the Einstein temperatures $\vartheta_{Ei}(1)$ and the weights $g_{Ei}(1)$ were taken from the spectroscopic data. They are as follows (in degrees Kelvin with the weight given in parentheses); 4800(6), 4600(6), 2351(6), 1220(3), 1206(3), 1148(1), 1128(1), 1032(4), 902(3), 888(3), 682(3), 665(2), 614(3), 530(4), 530(1), 374(3), 366(3), 317(2), 229(3). Site and factor group splittings were ignored, because their effect on the heat capacity was insignificant as long as the total number of the modes were counted correctly in each of the multiplets. C(1) was calculated using the following equation:

$$C(1) = R\sum_{i=1}^{N_E(1)} g_{Ei}(1) C_E(\Theta_{Ei}(1)/T) \tag{1}$$

where R is the gas constant and C_E the Einstein heat capacity function normalized to 1 at $T=\infty$,

$$C_E(x) = x^2 e^{-x}/(1-e^{-x})^2 \tag{2}$$

In total 60 degrees of freedom were included in C(1).

The term C(2) containing unknown characteristic temperatures was as follows:

$$C(2) = R\sum_{i=1}^{N_E(2)} g_{Di}(2) C_D(\Theta_{Di}(2)/T) + R\sum_{i=1}^{N_E(2)} g_{Ei}(2) C_E(\Theta_{Ei}(2)/T) \tag{3}$$

where $g_{Di}(2)$ and $g_{Ei}(2)$ are the weights of the contributions from the respective terms. They were chosen to properly represent the vibrational units in accordance with the known spectroscopic and structural properties of the molecular ions. $\vartheta_{Di}(2)$ and $\vartheta_{Ei}(2)$ are the Debye and Einstein temperatures to be optimized by the least squares method to reproduce the experimental heat capacities. The sum of the weights $g_{Ei}(1)$ ($i = 1$ to $N_E(1)$), $g_{Di}(2)$ ($i = 1$ to $N_D(2)$) and $g_{Ei}(2)$ ($i = 1$ to $N_E(2)$) is equal to the number of the vibrational degrees of freedom. Since there are $N = 27$ atoms in the chemical unit $Co(H_2O)_6(BrO_3)_2$ they sum up to 81. Thus

$$3N = \sum_{i=1}^{N_E(1)} g_{Ei}(1) + \sum_{i=1}^{N_D(2)} g_{Di}(2) + \sum_{i=1}^{N_E(2)} g_{Ei}(2) \tag{4}$$

We chose $N_D(2) = 1$, $g_{D2}(1) = 3$; $N_E(2) = 3$, $g_{E1}(2) = 6$, $g_{E2}(2) = 9$, $g_{E3}(2) = 3$. The first term contains 60 degrees of freedom, the second term 3 and the third term 18.

The Debye function was computed by the use of a series expansion [38],

$$C_D = \frac{4}{5}\frac{\pi^4}{x^3} - \sum_{n=1}^{\infty}\left(3(nx) + 12 + \frac{36}{nx} + \frac{72}{(nx)^2} + \frac{72}{(nx)^3}\right)\frac{e^{-nx}}{n} \tag{5}$$

where $x = \vartheta_D/T$. The infinite series was truncated in the actual calculation at an appropriate number of terms.

The C_p–C_v correction term was included in the calculation in the form AC_p^2T where A was one of the least squares parameters. This has a thermodynamic basis in the quasi-harmonic approximation [39].

3.2. Optimization and its result

The parameters $\vartheta_{Di}(2)$ ($i = 1$), $\vartheta_{Ei}(2)$ ($i = 1$–3) and A were optimized by minimizing the following function:

$$F(\Theta_{D1}(2), \Theta_{E1}(2), \Theta_{E3}(2), A) = \sum_{i=1}^{N_{DA}} \{C_{exp}(T_i) - C_{calc}(T_i)\}^2 \tag{6}$$

$$C_{calc}(T_i) = C(1) + C_{sch} + C(2) + A(C_{exp}(T_i))^2 T_i \tag{6a}$$

where N_{DA} is the number of the experimental points taken into the fitting. The second term in Eq. (6a) accounts for the electronic energy levels due to the spin orbit coupling in the cobalt(II) ion. Its small contribution to the heat capacity was calculated by the Schottky equation using the coupling constant $\lambda = 180\ cm^{-1}$ [40].

The search for the best-fit parameter values was performed on a personal computer for

Table 3

The best-fit values of the Debye and Einstein temperatures and the A coefficient determined from the 13–200 K data set

$\Theta_D(3)$/K	$\Theta_E(6)$/K	$\Theta_E(9)$/K	$\Theta_E(3)$/K	A/mol J^{-1}
92.7 ± 0.7	123.6 ± 0.5	231.0 ± 0.4	614 ± 10	(5.76 ± 1.0)E–7

which the program was written in BASIC. The algorithm was based on iterated solution of the linearized normal equation. With five parameters to be optimized for 100 data points, one cycle of calculation took about 30 s. Therefore, various initial values could be tested without consuming too much time. The least squares program was originally written in FORTRAN to be run on a main-frame computer. It was translated to BASIC as fast personal computers became available later.

The best-fit functions are shown in Fig. 1 along with the experimental points. Table 3 gives the best fit set of the parameter values based on the data points between 13 and 200 K. The Debye term ($\vartheta_{D1}(2) = 92.7$ K) represents the acoustic branch of the lattice vibration and the Einstein terms the optical branches, i.e. relative motions (rotational and translational) of the molecular ions. The highest frequency mode $\vartheta_{E3}(2)$ (= 600–770 K) represents a part of the torsional modes of the water molecules, while $\vartheta_{E1}(2)$ (= 123.6 K) and $\vartheta_{E2}(2)$ (=231.0 K) may be identified with translational and rotational parts, respectively, of the optical modes. However, precise correspondence should not be expected to hold between such qualitative description of the lattice vibration and the actual characteristic temperatures.

The weights of the modes may be justified as follows. The Debye term has a weight of three as usual to represent the longitudinal and two transverse modes of the acoustic vibration. The weight 6 of $\vartheta_{E1}(2)$ may be identified with three (i.e. x, y and z) translations of each of the two bromate ions. The weight 9 of $\vartheta_{E2}(2)$ was at first divided as 6 + 3 and meant to represent six rotational vibrations of the two bromate ions and three rotational vibrations of the cobalt hexahydrate ion. The least squares calculation based on this model function gave close values for the two characteristic temperatures. Therefore, they were put together with a combined weight of 9 assigned to it. The residual value of F (Eq. 6) obtained with the simplified model was no larger than that from the original model. Therefore, it was accepted in the final result.

There are several Raman lines in the corresponding frequency region (Table 2). They may be identified with the calorimetric Einstein frequencies, 83 cm^{-1} (123 K) and 160 cm^{-1} (230 K). In view of the averaging nature of the thermodynamic measurement, the agreement between the two results is satisfactory. Thus the detailed lattice vibrational spectra (Fig. 3) are averaged into a small number of the Einstein and Debye temperatures.

One may ask how faithfully the least squares parameters represent the actual lattice spectrum of the complex crystal. In order to answer this question, we varied the temperature interval of the data taken into the least squares calculation. If the model function was an accurate representation of the actual lattice spectrum, the parameter values would be stable against the variation of the data set used for the fitting. This was actually the case.

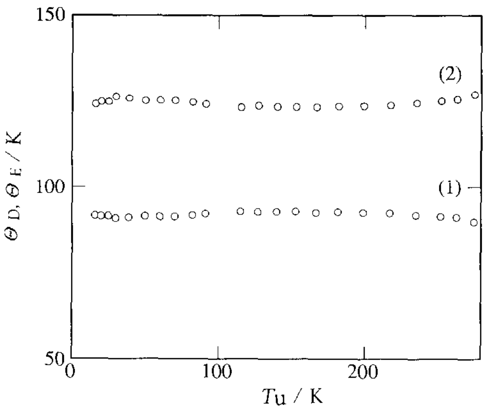

Fig. 4. The best-fit Debye (1) and Einstein (2) temperatures as functions of the data set used for the fitting. The horizontal axis represents the upper end temperature of the interval of the data set. The lower end temperature was 13 K for all of the points. Probable errors are roughly equal to the size of the circles.

Figs. 4 and 5 show the best-fit parameter values as functions of the upper limit temperature T_u of the fitting interval. The lower limit was fixed to 13 K for all the points plotted. Thus, the data points plotted at 16 K were calculated using the experimental heat capacities between 13 and 16 K, those at 20 K were calculated using the heat capacities between 13 and 20 K and so on. The Debye temperature and two low Einstein temperatures are remarkably constant against the change in the data set used for the fitting. This gives strong credibility to the fitting procedure. The highest Einstein temperature (curve (1) of Fig. 5) and the A coefficient (Eq. 6a) are correlated in the least squares fitting. Also these two terms contribute only weakly for $T < 150$ K. These factors, coupled with the small

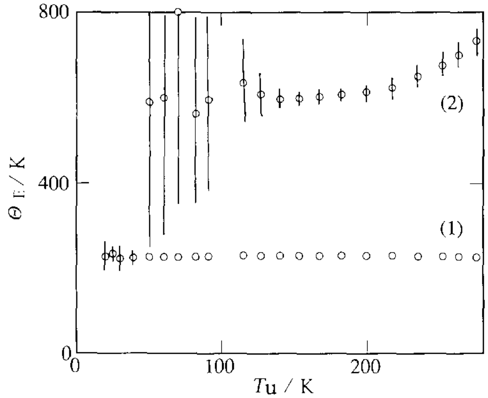

Fig. 5. The best Einstein temperatures as functions of the data set used for fitting. The horizontal axis gives the upper end temperature of the interval of the data set. The lower end temperature was 13 K for all of the points. Probable errors are given by the vertical bars for the upper curve and for some of the points in the lower. For those without an error bar the probable error is roughly equal to the size of the circle.

weight 3 of the highest Einstein temperature, made the last two parameters less accurate than the others.

3.3. Debye temperature from the elastic properties

The Debye temperature is related to the sound velocities by the following equation [39]:

$$\Theta_D = \frac{h}{k}\left\{\frac{9N_0}{4\pi V}\frac{1}{(1/c_l)^3 + 2(1/c_t)^3}\right\}^{1/3} \tag{7}$$

where h and k are the Planck and Boltzmann constants, V the volume of the elastic continuum and N_0 the number of particles (atoms or molecules) assumed to form the continuum. c_l and c_t are the longitudinal and transverse sound velocities, respectively. They are related to the elastic constants by the following equations [39]:

$$c_l = \sqrt{c_{11}/\rho} \tag{8}$$

$$c_t = \sqrt{c_{44}/\rho} \tag{9}$$

where ρ is the mass density = 2.53 g cm^{-3} [28]. The elastic constants [30] are $c_{11} = 2.200 \times 10^{10}$ N m^{-2}, $c_{12} = 1.088 \times 10^{10}$ N m^{-2} and $c_{44} = 0.854 \times 10^{10}$ N m^{-2} at 298 K. The Debye temperature calculated from these values is 92.4 K. It agrees very well with the value from the heat capacity. If the elastic and volume data for 250 K is used, we obtain a Debye temperature of 95.4 K. Being a mechanical quantity, it depends on the temperature only weakly, but the small increase agrees with the general property of solids that they become stiffer at lower temperature.

The quantity N_0/V in Eq. (7) is rather interesting. This is the number density of the vibrating units (atoms or molecules) and, as such, has an obvious meaning for monatomic and other simple substances. For the present crystal, it is not obvious whether we should count the number density by (1) the individual ions, (2) the chemical unit or (3) the cubic unit cell. The first, second and third choices gave 134 K, 92 K and 59 K for the elastic Debye temperature. The second choice agrees with the calorimetric Debye temperature. This indicates that the vibrating unit consists of a cobalt hexahydrate cation and two bromate anions. This agrees with the basis of the calorimetric analysis that employs the chemical unit.

In the analysis of the heat capacity of solids, it has been standard practice to define limiting Debye temperatures at high and low temperatures [41]. The former gives a measure of the frequency range of the entire lattice spectrum. The latter is related to the sound velocity and elastic constants. Therefore, comparison between thermal and elastic Debye temperatures has previously been made by taking the low temperature limiting value of the thermal Debye temperature. In the present analysis, the Debye temperature remains at a constant value at all temperatures from well above the Debye temperature down to the lowest temperature (13 K), as shown in Fig. 4. Thus the comparison between thermal and elastic Debye temperatures was made directly, the low temperature extrapolation being unnecessary. The Debye temperature determined in the present analysis is the low-temperature Debye temperature even when it was determined from a data set covering the whole temperature range.

The C_p–C_v term was typically 23 J $K^{-1}mol^{-1}$ at 250 K, or 5.8% of C_p. The best-fit value of the correction coefficient A was (2–5) × 10^{-7} mol J^{-1} depending on the T_u value. This quantity is related to the thermal expansivity and elastic constants c_{ij} by the equation [42]

$$C_p - C_v = TV\sum_{ij} \alpha_i c_{ij} \alpha_j = TV(3c_{11} + 6c_{12})\alpha^2 \tag{10}$$

Substituting appropriate values for a and c_{ij} from Ref. [30] and equating the result with AC_p^2T, we obtained $A = (3.48 \pm 0.05) \times 10^{-7}$ mol J^{-1} at 250 K. The agreement with the calorimetric value is satisfactory. The probable error of A from the calorimetry is much larger than that of the elastically determined value. This is because the $C_p - C_v$ difference is a correction term of small magnitude and thus could not be determined accurately from the calorimetric data.

In the present analysis, all the experimental points were given the same weight in the least squares fitting. This may be modified by various weighting schemes, in order to take into account the different accuracy and precision of the heat capacity data at different temperatures. Weighting will be necessary when we analyze heat capacities below 10 K where the magnitude of the heat capacity depends strongly on the temperature. But in such a low temperature region, a different fitting scheme utilizing the T^3 dependence will be applicable. For the temperature region dealt with here, the even weighting worked well.

4. Conclusion

It has been customary to derive the Debye T^3 part from C_p data by plotting C_p/T against T_2, the slope being proportional to the magnitude of the Debye term. This method is particularly suitable for analysis of the heat capacity of a metal for which the T term is also of interest. Another way often taken is to calculate the Debye temperature from the heat capacity data as a function of temperature [43]. For this purpose one has to normalize the heat capacities judiciously. If the crystal were an ideal Debye solid, the Debye temperature thus determined should be constant against the temperature. This is not the case for actual substances and the Debye temperature depends on the temperature. One may interpolate the Debye temperature curve into an anomalous region, if there is one, to determine the excess heat capacity, a most recent use of the Debye function for this purpose being found in Ref. [44]. One may also discuss its temperature dependence by invoking contributions from narrow-band optical modes that may be inferred to exist from the molecular and crystal structures. The calculation presented in this paper is an attempt to systematize and simplify the use of the Debye and Einstein functions and thereby to allow different model functions to be tested against the experimental data. The final result obtained is in quantitative agreement with the independent data on the elastic property. Other parameters determined in the fitting (optical branch frequencies and the $C_p - C_v$ correction coefficient) are related with spectroscopic and thermal expansivity data. They are compared favorably for the present compound. Elastic, spectroscopic and expansivity data may not be available for other compounds, but the present result suggests that the same method will give a reliable estimate of the vibrational heat capacity of substances whose excess heat capacity one would like to extract from the experimental data.

Appendix

Standard thermodynamic functions were calculated from the heat capacity data and are given in Table A1.

Table A1

Standard thermodynamic functions of $Co(CH_2O)_6(BrO_3)_2$ crystal (R = 8.31451 J K^{-1} mol^{-1})

T/K	$C_p°/R$	$(H°-H_0°)/RT$	$(S°-S_0°)/R$	$-(G°-H_0°)/RT$
5	0.0378	0.0096	0.0132	0.0481
10	0.2855	0.0734	0.0998	0.0253
15	0.8678	0.2317	0.3151	0.0826
20	1.738	0.4955	0.6795	0.1840
25	2.790	0.8467	1.177	0.3310
30	3.988	1.269	1.791	0.5216
35	5.278	1.749	2.502	0.7529
40	6.600	2.273	3.293	1.020
45	7.964	2.829	4.149	1.320
50	9.327	3.411	5.059	1.648
60	11.99	4.620	6.996	2.376
70	14.51	5.855	9.036	3.181
80	16.89	7.086	11.13	4.044
90	19.14	8.301	13.25	4.949
100	21.26	9.492	15.38	5.885
110	23.27	10.65	17.50	6.844
120	25.18	11.79	19.61	7.821
130	27.00	12.89	21.69	8.807
140	28.74	13.96	23.76	9.802
150	30.42	15.00	25.80	10.80
160	32.03	16.01	27.81	11.80
170	33.59	17.00	29.80	12.80
180	35.11	17.97	31.77	13.80
190	36.59	18.91	33.71	14.80
200	38.04	19.83	35.62	15.79
210	39.47	20.73	37.51	16.78
220	40.86	21.61	39.38	17.76
230	42.24	22.48	41.22	18.74
240	43.60	23.33	43.05	19.72
250	44.95	24.17	44.86	20.69

Table A1 (*continued*)

T/K	$C_p°/R$	$(H°-H_0°)/RT$	$(S°-S_0°)/R$	$-(G°-H_0°)/RT$
260	46.27	24.99	46.65	21.65
270	47.58	25.81	48.42	22.61
273.15	47.99	26.06	48.97	22.91
280	48.88	26.61	50.17	23.56
290	50.15	27.40	51.91	24.51
298.15	51.17	28.03	53.31	25.28
300	51.40	28.18	53.63	25.45
310	52.63	28.95	55.33	26.39

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