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Thermodynamical properties of K_2OsCl_6 and K_2ReCl_6 at low temperatures and near their structural phase transitions*

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Specific-heat measurements on K_2OsCl_6 single crystals revealed anomalous behavior at low temperatures. The specific heat of the acoustic modes corresponds to a Debye temperature Θ_D of 63.6 ± 0.2 K. The contribution of low-lying optical modes including a rotary mode extend the description of the specific heat by the cubic law up to $T/\Theta_D \simeq 1/6$. A small anomaly of unknown origin occurs, however, at $T = 6.67 \pm 0.05$ K. The specific heat and entropy of K_2ReCl_6 and K_2OsCl_6 evaluated using the technique of the special points in the Brillouin zone agree well with experimental values outside of the regions of structural phase transitions at 103.4 and 110.9 K in K_2ReCl_6 and 46.1 K in K_2OsCl_6. These calculations permit the evaluation of excess entropies and specific-heat discontinuities associated with the transitions. The critical behavior around the structural phase transition at 46.1 ± 0.5 K in K_2OsCl_6 is also discussed. It is concluded that the range of the interaction associated with the transition is approximately the interoctahedral separation.

I. INTRODUCTION

Although considerable progress has been made in the general understanding of structural phase transitions in recent years, many theoretical and experimental aspects of the instabilities of certain lattice displacement modes are not well resolved. Until recently, displacive phase transitions including ferroelectric, antiferroelectric, and purely displacive types were frequently characterized in terms of Landau's theory of second-order transitions in conjunction with the concept of a soft phonon mode.[1-3] The frequency of this mode decreases rapidly near the critical temperature as though the restoring force responsible for that mode softens. However, many of the dynamical properties could not be completely understood on the basis of a mean-field theory and the concept of fluctuations was introduced.[2-4] These fluctuations are thought to result in the appearance of a central peak in the dynamic form factor $S(\vec{q}, \omega)$ and several microscopic theories have been proposed to account for this phenomenon.[5-10] Many experimental investigations of substances exhibiting structural phase transitions[11-15] have already been reported. An interesting class of materials which exhibit structural phase transformations are materials of the R_2MX_6 class where R, M, and X are alkali, metal, and halide atoms, respectively. The best studied compound of this class, K_2ReCl_6, has purely displacive transitions at $T_{c3} = 103.4$ K and at $T_{c4} = 110.9$ K which are believed to have associated soft modes, a first-order transition at $T_{c2} = 76.5$ K and an antiferromagnetic transition at $T_{c1} = 11.9$ K.[16,17]

Many thermodynamic and dynamic properties of the system can be determined from the dynamic form factor, $S(\vec{q}, \omega)$ which can be measured by inelastic neutron scattering. This technique can also provide vertification of a soft phonon picture. However, the complexity inherent in the description of cooperative phase transformations requires extensive experimental investigation with many other techniques such as infrared absorption, Raman scattering, correlation spectroscopy, x-ray scattering, magnetic resonance, thermal expansion, and specific heat in order to provide a complete understanding of the microscopic processes involved in the transitions.

The specific heat has been measured for several compounds of the R_2MX_6 class[16,18-21] including K_2ReCl_6. Here we report measurements of the specific heat of K_2OsCl_6. This compound exhibits a structural phase transition near 45 K as observed previously by nuclear quadrupole resonance.[22] Our primary objective was to obtain a measure of the excess entropy associated with the transition and the specific-heat scaling-law parameter α. In addition, the specific heat at low temperature had not been reported for an R_2MX_6 compound and therefore it was decided to carry out a careful low-temperature investigation of K_2OsCl_6. Finally, a reassessment of the available K_2ReCl_6 data was undertaken in conjunction with the analysis of the K_2OsCl_6 data.

We will briefly outline some of the experimental aspects and present the results obtained for K_2OsCl_6 in Sec. II. In Sec. III we describe the calculation of the specific heat and entropy of K_2ReCl_6 and K_2OsCl_6 using the method of special points in the Brillouin zone. The behavior in the critical region is discussed in Sec. IV.

II. EXPERIMENTS AND RESULTS

R_2MX_6 compounds exhibit the cubic antifluorite structure at high temperatures[23] and thus belong to the O_h^5 space group. The MX_6 octahedra composed of an M ion in the center and X ions at the vertices form an fcc lattice. The R ions form a cubic cage around the octahedra such that the X ions almost lie in the center of the cube (100) faces. The intraoctahedral bonds have a significant covalent character.

The important property of MX_6 octahedra is that they behave as rigid entities both in solid and solution. Solid body rotations of the octahedra which are related to the rotary modes are believed to play an important role in inducing the transitions T_{c3} and T_{c4} in K_2ReCl_6 and the transition in K_2OsCl_6. The amount of static rotation is taken as the order parameter. The important forces are the attractive R-X and the repulsive interoctahedral X-X interactions.

Single crystals of K_2OsCl_6 were used in the measurements, the amount of material in any crystal not exceeding 7×10^{-4} moles.

The measurements were performed by the discontinuous-heating method with temperature intervals less than 0.05 of the temperature. In the vicinity of the phase transitions, typical temperature intervals of 0.01 of the temperature or less were employed. The apparatus used in these measurements has been described elsewhere.[24] The only notable changes were in the calorimeter assembly which was made from a silicon chip, a 1-mg germanium thermometer, and a 4000-Ω evaporated heater. The samples were mounted onto the calorimeter with Apiezon T grease. In the temperature range 1–15 K the thermometer calibration was checked by measuring the specific heat of copper and was in agreement with the standard within 0.4%.[24] Above 15 K, the calibration was performed with a GaAs diode.[25] When thermal nonequilibrium is not significant, the accuracy of the measurements is ±2% between 15 and 60 K. In these measurements thermal nonequilibrium appeared above 10 K and the thermal relaxation time increased with increasing temperature. In this temperature range the data were analyzed using a method similar to that described in Ref. 24 and the estimated uncertainty of the specific heat is less than ±3%. The heat capacity of the calorimeter was determined in separate measurements and accounted for only a small portion (< 5%) of the total heat capacity. Thermal nonequilibrium was traced to the low thermal conductance of the grease-crystal interface. Moreover this conductance decreased with time or cycling and thus Apiezon T grease is not recommended for thermal contact to compounds of the R_2MX_6 class.

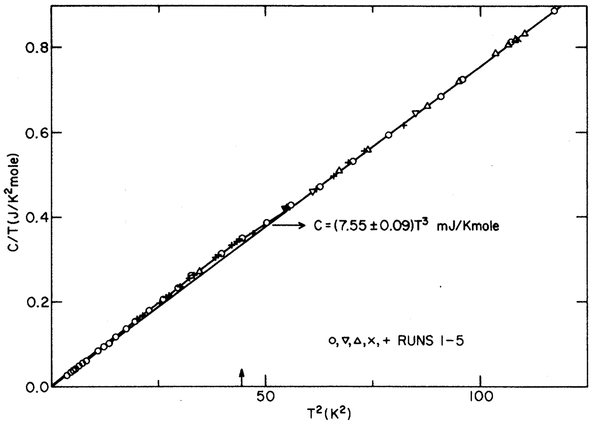

FIG. 1. Specific heat C of K_2OsCl_6 between 1.5 and 12 K plotted as C/T vs T^2.

The specific-heat results of K_2OsCl_6 are shown in Figs. 1 and 2 and tabulated in Table I together with the entropy. The specific heat may be represented with a high-order polynomial and the entropy calculated from $S(T) = \int_0^T [C(T')/T'] dT'$. Several unexpected features are apparent in Figs. 1 and 2. A small low-temperature anomaly is observed at 6.67±0.05 K. This anomaly cannot be associated with the heat capacity of the calorimeter. The addenda contributes only 1% to the measured heat capacity in this temperature range, it does not exhibit any anomaly and is accounted for by the heat capacity of the calorimeter components. The low-temperature heat capacity is

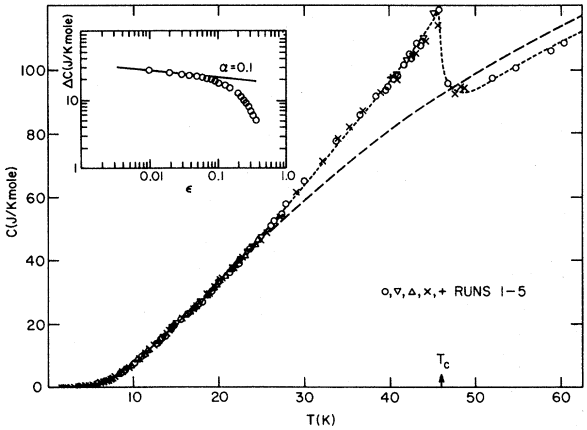

FIG. 2. Specific heat C of K_2OsCl_6 between 1.5 and 60 K. The dashed line represents the background specific heat calculated using the technique of special points in the Brillouin zone. The inset shows the scaling plot of the excess specific heat ΔC vs $\epsilon = |T_c - T|/T_c$ below T_c. The scaling parameter $\alpha \simeq 0.1$ ($\Delta C \sim \epsilon^{\alpha}$) is schematically indicated.

TABLE I. Specific heat C and entropy S of K_2OsCl_6 between 1.5 and 60 K.

T (K)	C (J/K mole)	S (J/K mole)
1.5	0.0264	0.0088
2.0	0.0626	0.021
3.0	0.212	0.0705
4.0	0.502	0.167
5.0	0.983	0.327
$T_{c1}=6.67$	2.34	0.778
7.5	3.17	1.10
10.0	7.50	2.55
12.5	13.7	4.90
15.0	20.0	7.99
20.0	33.3	15.5
25.0	47.8	24.4
30.0	63.5	34.5
35.0	79.9	45.5
40.0	95.9	57.3
45.0	113.7	69.5
$T_{c2}=46.1$	118.7	72.3
50.0	94.7	80.2
60.0	108.0	98.6

anomalously large and leads to a Debye temperature $\Theta_D = 63.6 \pm 0.2$ K. At the same time the cubic dependence of the specific heat extends to ~11 K, i.e., $\frac{1}{6}\Theta_D$ excluding the enhancement around 6.67 K. The specific-heat anomaly in the vicinity of the structural phase transition extends over a considerable range below 46.1 K and thus leads to a large excess of specific heat and hence a large excess entropy.

Excluding the low-temperature anomaly, the specific heat below 11 K can be well represented by $C = (7.55 \pm 0.09)T^3$ mJ/K mole. C is well described by the cubic law over an anomalously large temperature range because of the contribution of low-frequency optical modes and can be accounted for as shown in Sec. III. The low-temperature anomaly has an excess entropy of ~0.040 J/K mole and a latent heat of 0.19 J/mole. If the anomaly is associated with a two-level system having equal degeneracy, we obtain an energy splitting of 11 cm^{-1} between the upper and lower states. The fractional number of these two level sites per number of chlorine sites would be $\sim 5\times 10^{-3}$. Since nuclear-magnetic-resonance studies revealed a significant proton concentration, the anomaly may be related to their presence.

III. SPECIFIC-HEAT CALCULATIONS

The lattice specific heat at constant volume is given by the expression

$$C_v = k_B \sum_{\vec q} \frac{x^2 e^x}{(e^x - 1)^2} \quad \text{with } x = \hbar\omega_{\vec q}/k_B T. \tag{1}$$

The summation is carried out over all the phonon modes $\omega_{\vec q}$ and T is the sample temperature. The technique of using certain special points in the Brillouin zone (BZ)[26,27] permits the approximate evaluation of the average of any periodic function of wave vector. This technique has been used to calculate the average value of the angular vibrational amplitude of the Re–Cl bond in K_2ReCl_6.[28] We employ this technique to calculate the contribution of all optical modes to the specific heat and entropy of K_2ReCl_6 and K_2OsCl_6. The difference between the calculated and measured specific heat in the transition region serves as the estimate of the excess specific heat and entropy associated with each of these transitions. The special points are defined as the points where the values of any periodic function of wave vector are a good approximation to the average value of this function over the BZ. The periodic function of the wave vector $f(\vec q)$ can be expressed in the form

$$f(\vec q) = f_0 + \sum_{m=1}^{\infty} f_m A_m(\vec q) = f_0 + \sum_{m=1}^{\infty} f_m \sum_{|\vec R| = C_m} e^{i\vec q\cdot\vec R}, \tag{2}$$

where the summation over $|\vec R|$ runs over equivalent lattice vectors related to each other through the operations of the lattice-point group. The average $\bar f$ over the BZ is defined as

$$\bar f = \frac{V_c}{(2\pi)^3}\int_{\text{BZ}} f(\vec q)\, d\vec q\,, \tag{3}$$

where V_c is the primitive cell volume. Substituting (2) into (3), one obtains $\bar f = f_0$. The average could be readily obtained if there existed a point $\vec q_0$ where $A_m(\vec q_0) = 0$ for any positive integer m, since then $\bar f \equiv f_0 \equiv f(\vec q_0)$. Such a point does not exist, but the expansions (2) are usually rapidly convergent so that a good approximation can be obtained if the weighted summation of $A_m(\vec q_i)$ is equal to zero for the highest m possible using several special points $\vec q_i$. The average $\bar f$ is then the weighted sum of $f(\vec q_i)$'s. The best single point for the fcc lattice is $\vec q_1 = (2\pi/a)(0.6223, 0.2953, 0)$; the best two-point scheme is

$$\vec q_1 = (2\pi/a)(\tfrac34, \tfrac14, \tfrac14), \quad \vec q_2 = (2\pi/a)(\tfrac14, \tfrac14, \tfrac14), \tag{4}$$

with weighting factors 3 and 1, respectively.

The specific heat for K_2ReCl_6 is evaluated as the sum of the contribution of acoustic modes given by the Debye approximation and the contribution of optical modes determined by the special-points technique. The phonon frequencies at the special points are determined on the basis of the rigid-ion lattice-dynamical calculation of O'Leary and Wheeler.[17] Their model assumes that the rigid (nonpolarizable) ions interact with forces which can be divided into a large-range Coulomb part due to the ionic charges and a short-range part due to the overlap of the electron distribution of neighboring ions. Ionic charges and force constants are evaluated by fitting the spectroscopically observed phonon frequencies.

The following assumptions are made: (i) the phonon frequencies of the distorted phases can be approximated by those of the fcc phase and (ii) the frequencies are temperature independent, including the acoustic frequencies which define the Debye temperature.

The Debye temperature Θ_D of K_2ReCl_6 cannot be inferred from the data because the measurements were not carried out to low enough temperatures and because of the presence of the low-temperature magnetic transition at 11.9 K. Therefore, Θ_D of K_2OsCl_6 is taken in the calculation. Furthermore, the lowest-lying optical modes, the rotary modes associated with the solid body rotations of the MX_6 octahedra, are altered to provide agreement with the experimental specific heat around 25 K. These modes are observed to be extremely sensitive to small changes in the force constants and ionic charges. The frequencies employed in this calculation, $\omega_{RT} = 44$ cm^{-1} and $\omega_{RL} = 49$ cm^{-1} actually lie between those determined by models I and II.[17] Calculations employing one and two special points were performed. The largest deviations between the one- and two-special-point schemes occurred, as expected, at the lowest temperatures, but here the specific heat is dominated by the acoustic modes, so that the total values calculated with a one- or two-point scheme do not differ by more than 1% over the whole temperature range. Good agreement between the one- and two-point schemes is expected because of the low dispersion of the majority of the optical modes. The results are shown in Table II together with experimental values. Excellent agreement, within the accuracy of the specific-heat measurements, is found over the whole temperature range with the exception of the transition regions between 7 and 25 K and between 60 and 120 K. The calculated background entropy permits an estimate of the excess entropies associated with the transitions. For the transitions at 76.05, 103.4, and 110.9 K the excess entropies are 0.9, ~0.7, and ~0.7 J/K mole, respectively. This is in contrast with the earlier rather questionable estimates of $R \ln 2 = 5.76$ J/K mole per transition.[16] The discontinuities in the specific heat at the above transitions are 11.2, 12.8, and 10.3 J/K mole, respectively.

Even though spectroscopic data similar to that for K_2ReCl_6 are not available for K_2OsCl_6, the good agreement for K_2ReCl_6 encouraged us to attempt similar calculations for K_2OsCl_6. With the exception of the small anomaly in C at $T_c = 6.67$ K no other transition occurs below 30 K, so that special-point frequencies of the lowest-lying optical modes can be roughly estimated in order to account for the observed specific heat. The eight lowest modes of K_2OsCl_6 were shifted to somewhat lower frequencies compared with K_2ReCl_6 while the remaining K_2ReCl_6 frequencies were employed unchanged. The set of frequencies was probably not determined uniquely; therefore we quote only the frequency of the rotary mode at the point $\vec{q}_1$, namely, $\omega_{RT} = 47$ cm^{-1}. The calculated specific heat shown in Fig. 2 deviates by less than 5% from the experimental values, away from the transition region; this can be considered reasonable agreement bearing in mind that the phonon frequencies are not well known. The excess entropy associated with the 46.1-K transition is ~6.6^{-1}_{+3} J/K mole. This estimate is rather inaccurate because the transition extends over a large temperature range and therefore even a small deviation of the specific heat will lead to a large change in the background entropy. The specific-heat jump at the structural phase transition is ~27.2 J/K mole.

TABLE II. Specific heat of K_2ReCl_6 calculated using the technique of special points in the Brillouin zone and the measured specific heat. The deviations occur only around structural phase transition T_{c4}, T_{c3}, T_{c2} and around the antiferromagnetic transition T_{c1}.

T (K)	C_{calc} (J/K mole)	C_{exp} (J/K mole)
10.0	7.23	15.2
$T_{c1} = 11.9$	11.15	41.8
20.0	29.9	31.2
30.0	53.4	53.9
40.0	75.3	75.3
50.0	94.5	94.7
60.0	110.7	111.2
$T_{c2} = 76.05$	131.6	142.7
80.0	136.1	138.0
100.0	154.6	161.0
$T_{c3} = 103.4$	157.3	170.1
$T_{c4} = 110.9$	162.7	173.1
120.0	168.7	168.7
140.0	179.3	178.8
160.0	187.3	187.0
180.0	193.7	193.8
200.0	198.5	199.0
250.0	206.8	208.4
300.0	211.8	214.9

IV. DISCUSSION OF CRITICAL BEHAVIOR

In this section, we will examine some aspects of the behavior of the specific heat around the 46.1-K transition in K_2OsCl_6 and the 103.4- and 110.9-K transitions in K_2ReCl_6. It was hoped that a determination of the excess entropy associated with these transitions would give a clear indication of the nature of the transitions. In a second-order transition, the symmetry changes continuously while in a first-order transition, there is a discontinuous jump from one symmetry to the other. Generally, the excess entropy associated with second-order displacive phase transitions has been observed to be less than 0.1 J/K mole; however, there is no need for it to be this small.

Measurements and calculations of the background specific-heat yield excess entropies of ~0.7 J/K mole for both the 103.4- and 110.9-K transitions. It is generally agreed that these transitions are second-order displacive transitions associated with the X-point and Γ-point soft modes, respectively.[17] The 46.1-K transition in K_2OsCl_6 has an estimated excess entropy of 6.6 J/K mole which is close to $R\ln 2$ within the accuracy of the present evaluation.

The hysteresis usually associated with the metastable states of first-order transitions was not observed in these measurements. It is reasonable to conclude that the transition in K_2OsCl_6 is not first order, but it is possible that it could be order disorder rather than purely displacive. An excess entropy of $R\ln 2$ suggests the possibility that above T_c two distinct orientations of the $OsCl_6$ ions are equally likely, but below T_c one of them is frozen out. The simple antifluorite structure requires that the angle ϕ between the axis of the octahedra and the cubic potassium cage is equal to zero. This position, however, does not have to correspond to a minimum in the electrostatic potential energy. A combination of attraction and repulsion between cations and anions and between octahedra could produce two minima in the potential energy symmetrical about $\phi = 0$.

In a transition of second order, the mean displacements must increase continuously from zero and therefore there will be a region near the transitions where thermally excited fluctuations in the atomic positions may be larger than the mean displacements. This temperature interval is called the critical region and it is desirable to have an estimate of the size of this region.

Empirically we can define the critical region as the temperature interval in which the specific-heat scaling law parameter α reaches a reasonable value, for example, $\alpha < 0.1$. The parameter α is related to the excess specific heat ΔC by the relation $\Delta C = \epsilon^{\alpha}$, where $\epsilon = |T_c - T|/T_c$. As the scaling plot shown in the inset of Fig. 2 indicates, this would be roughly satisfied for $\epsilon < 0.01$, that is, for $T_c - T < 0.5$ K. Furthermore, it should be recalled that Landau's theory predicts a single discontinuity in C for a second-order phase transition. The transition at 46.1 K thus demonstrates a deviation from mean-field behavior. According to Ginzberg[29] the zero-temperature coherence length l is related to the discontinuity in the specific heat δC by

$$l = (k_B/\rho\delta C)^{1/3}\epsilon_c{}^{-1/6} , \qquad (5)$$

where ϵ_c is the fractional temperature range over which deviations from mean-field behavior are observed and ρ is the density. The estimate (5) strictly applies only in cases of relatively long-range electrostatic forces and a small change in the free energy accompanying the transition.

The calculated background specific heat permits us to evaluate the discontinuities $\delta C_{T_{c_3}} = 12.8$ J/K mole, $\delta C_{T_{c_4}} = 10.3$ J/K mole for K_2ReCl_6, and 27.7 J/K mole for K_2OsCl_6. Since $\epsilon_{c_3} \simeq 0.02$ and $\epsilon_{c_4} \simeq 0.01$, the estimates of the coherence lengths l_3 and l_4 are 10.2 and 12.5 Å, respectively. For K_2OsCl_6, $\epsilon_c \simeq 0.01$ and we obtain $l \simeq 9.0$ Å. We note that the estimates of coherence lengths for K_2ReCl_6 and K_2OsCl_6 are similar to the room-temperature lattice constants 9.86 and 9.73 Å, respectively, indicating that the important coupling is short range, that is, between neighboring octahedra.

For $T < T_c$, the anomaly C for K_2OsCl_6 extends over ~15 K. Such broadening is usually a consequence of internal stresses, compositional inhomogeneities or other extrinsic effects. It is interesting to point out that it shows up in the thermal expansion measurements for K_2OsCl_6 as well.[30] Apart from this similarity there is a difference between the specific-heat anomaly around T_c and the thermal expansion behavior. The thermal expansion peak is three times the background while the specific-heat discontinuity $\delta C/C$ is only about 25%. This difference is to be expected as the specific heat is equal to

$$C_v = \frac{d}{dT} \sum_{\vec{q}s} C_{ji}(\vec{q}s) \int_{-\infty}^{+\infty} \omega^2 S_{ij}(\vec{q}s, \omega) d\omega , \qquad (6)$$

where $S_{ij}(\vec{q}s, \omega)$ is the space and time Fourier transform of the displacement-displacement correlation function.

Because the frequency squared appears in the integrand, C is a less sensitive monitor of soft-mode or central-peak effects associated with structural transitions than the thermal expansion which depends on the integral of the function $S_{ij}(\vec{q}s, \omega)$ only. Therefore, the observation that the specific heat does not scale with the thermal expansion in the vicinity of the phase transition suggests the occurrence of a soft mode or central peak in K_2OsCl_6.

The temperature dependence of the specific heat in the critical region can often be analyzed in terms of the scaling laws to yield critical exponents.[31] In the present case the experimental results are not sufficiently detailed to extract critical exponents but do provide an upper limit of 0.1 for the scaling exponent below T_c.

In summary, the measurements of the specific heat of K_2OsCl_6 in the vicinity of the structural phase transition at 46.1 K have indicated that the transition is continuous, that the excess entropy is close to $R \ln 2$ within the experimental accuracy, that the coherence length is of the order of the interoctahedral separation, that there is a soft mode or central peak associated with the transition and that an upper limit for the scaling exponent below T_c is 0.1.

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