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Ferrorotative transition in the antifluorite crystal K_2OsCl_6

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The structural phase transition in potassium hexachloro-osmate (K_2OsCl_6) has been investigated at the NRU reactor, Chalk River, by elastic neutron-scattering methods. The observed change in the crystal structure in passing through T_c indicates that the $OsCl_6$ octahedra undergo a collective ferrorotation. The data are consistent with both a displacive and an order-disorder model. The transition occurs at $T_c = 44.5 \pm 0.4$ K and is continuous, with a critical exponent $\beta = 0.35 \pm 0.06$ characteristic of three-dimensional phase transitions.

I. INTRODUCTION

Many R_2MX_6 crystals, having the cubic antifluorite structure, exhibit structural phase transitions.[1] A comprehensive study of K_2ReCl_6 has been reported by O'Leary and Wheeler.[2] The transitions at 111 and 103 K in K_2ReCl_6 have been associated with the softening of rotary lattice modes at the zone center and zone boundary, respectively. Correspondingly the structural alterations associated with the two transitions are the result of static rotations of $ReCl_6$ octahedra whose symmetry is ferro- and antiferrorotative. Recent results on the isomorphous crystal K_2SnCl_6 suggest[3] that it has a single antiferrorotative transition. Structural transitions of this kind are often referred to as rotational phase transitions.

K_2OsCl_6 has a phase transition at ~45 K which is believed to be of the rotational type. Recent nuclear quadrupole relaxation measurements[4] suggest that it is the condensation of a rotary lattice mode which is responsible for the phase transition. The data indicates a critical slowing down of fluctuations in the rotation angle of $OsCl_6$ octahedra and the formation of dynamic clusters near T_c. Thermal expansion measurements[5] show that strain interactions must be included in a comprehensive description of the phase transition. Specific-heat measurements[6] have shown the excess entropy at the transition to be ~0.7 R and the coherence length is of the order of the interoctahedral separation. However, many questions concerning the nature of this phase transition remain unanswered. A comprehensive neutron scattering investigation has been undertaken to provide further information.

Although the structure of K_2OsCl_6 in the high-temperature phase has been determined by x-ray diffraction measurements,[7] there has been no study of the low-temperature structure. Therefore, as a first step, an elastic neutron-scattering experiment was undertaken to test the validity of the postulated rotational model and to establish whether the transition is ferro- or antiferrorotative. Further, the temperature dependences of two elastic peaks in the vicinity of T_c were studied to see if the transition is continuous, to obtain a more accurate value for T_c and to obtain the critical coefficient β, associated with the transition.

II. EXPERIMENT

Two single crystals, grown from aqueous solution,[8] about 1 cm^3 and 0.25 cm^3 in volume, were mounted and aligned so that the directions [110] and [001] defined the scattering plane. Most measurements were done on these crystals and in this plane. Some additional measurements were made on a third crystal (~1 cm^3) aligned with a $[\bar{1}30]$ axis vertical.

The experiments were carried out on the $L3$ triple axis spectrometer at the NRU reactor, Chalk River. The (113) plane of silicon was used as a monochromator and the incident neutrons had an energy of 10.00 THz. No analyzing crystal was used. The spectrometer collimations were 0.60° and 0.65° before and after the specimen.

Scans were made at several temperatures above and below T_c through zone centers and along zone boundaries. No superlattice reflections were observed below T_c along zone boundaries in the $(\bar{1}10)$ orientation, whereas certain of the zone center intensities exhibited large changes with temperature. These intensities changed continuously as the temperature was lowered below ~45 K. An antiferrorotative structural transition need not, however, produce observable satellites in the $(\bar{1}10)$ plane, as found by Boysen *et al.*[3] in K_2SnCl_6 who observed satellites at (312) and (532). Accordingly we searched at 20 K and 40 K in the $(\bar{1}30)$ scattering

plane for a possible (312) satellite but none was found. These results suggest that the transition is ferrorotative.

For the structure determinations, scans were made over 36 Bragg peaks in all four quadrants of the $(\bar{1}10)$ scattering plane. Radial scans were made at 298 K; radial and transverse scans at 4.6 K. Integrated intensities were deduced for each scan and the average intensity over the four quadrants was calculated. A dead-time correction was applied where necessary. The corrections for extinction and higher-order wavelength contamination are described later. No correction for absorption was made because the crystal dimensions were such that the correction was smaller than other sources of experimental error. The experimental integrated intensities I_i^{obs}, normalized so that

$$\sum_{i=1}^{N} \frac{I_i^{obs}}{N} = 1 ,$$

are given in Table I. The effective lattice parameters obtained from the Bragg peak positions at each temperature are quoted in Table II.

To determine the critical exponent β of the order parameter, the (117) and (337) reflections were measured at 25 temperatures in the range 4.6 to 58 K.

TABLE I. Comparison of the normalized integrated intensities of 36 Bragg peaks in K_2OsCl_6 at 298 and 4.6 K with the intensities calculated from the displacive model.

	298 K		4.6 K	
hkl	Measured	Calculated	Measured	Calculated
002	...	...	1.162	1.111
004	6.026	5.705	...	...
006	0.701	0.665	0.561	.627
008	3.158	2.917	3.109	3.564
0010	0.174	0.166	0.244	0.239
1111	0.008	0.003	0.112	0.108
119	0.573	0.590	0.421	0.488
117	0.020	0.017	0.147	0.174
115	0.997	0.935	0.565	0.597
113	0.390	0.370	0.308	0.278
111	...	...	0.476	0.487
220	0.053	0.057	0.054	0.063
222	4.432	4.718	4.206	3.929
226	2.261	2.269	2.438	2.612
228	0.041	0.033	0.025	0.016
2210	0.567	0.548	1.031	1.108
339	0.240	0.233	0.284	0.300
337	0.025	0.024	0.039	0.035
335	0.199	0.180	0.264	0.293
333	0.013	0.008	...	...
331	0.056	0.055	0.158	0.127
440	4.269	4.549	4.907	4.897
442	0.843	0.870	0.718	0.666
444	3.819	3.649	4.442	4.195
446	0.423	0.406	0.432	0.404
448	1.813	1.833	2.502	2.541
557	0.139	0.139	0.287	0.283
555	0.719	0.753	0.614	0.596
553	0.487	0.495	0.510	0.475
551	0.778	0.842	0.639	0.623
660	0.003	0.001	0.021	0.018
662	1.089	1.126	1.739	1.696
664	0.005	0.004	0.021	0.025
666	0.541	0.548	1.183	1.104
775	0.007	0.003	0.134	0.133
773	0.031	0.026	0.073	0.037
771	0.016	0.008	0.098	0.083
880	1.084	1.138	2.075	1.847

TABLE II. Parameters of the displacive model determined from the experimental intensities. The lattice parameter was measured independently, using the Bragg peak positions.

Parameter	298 K	4.6 K
$\langle\theta(\mathrm{Cl})\rangle$ (deg)	...	3.6 ±0.2
$\langle\theta^2(\mathrm{Cl})\rangle$ (deg^2)	17 ±1	3 ±1
$\langle u^2(OsCl_6)\rangle$ (Å^2)	0.014 ±0.002	0.037 ±0.002
$\langle u^2(\mathrm{K})\rangle$ (Å^2)	0.041 ±0.005	0.038 ±0.005
x_{Cl} (units of the lattice parameter)	0.2378±0.0003	0.2407±0.0005
g	0.0033±0.0003	0.0046±0.0007
$f(\frac{1}{2}\lambda)$	0.017 ±0.005	0.037 ±0.010[a]
Scale factor	0.056 ±0.003	0.127 ±0.007
Q	0.064	0.080
R	0.029	0.037
Lattice parameter (Å)	9.78 ±0.02	9.69 ±0.02
b_{Cl} (fm)	9.605 ±0.03	
b_{Os} (fm)	10.7 ±0.1	
b_K (fm)	3.71 ±0.02	

[a]The factor $f(\frac{1}{2}\lambda)$ is larger at 4.6 K by approximately the amount expected because an absorber was placed in the beam.

III. STRUCTURE ANALYSIS

The measured intensities were fitted to an expression of the form

$$I(\vec{H}) = \text{const} \times G(\theta) Y(\vec{H}) \left| F(\vec{H}) \right|^2$$
$$= \text{const} \times G(\theta) \left| F'(\vec{H}) \right|^2 ,$$

where the elastic scattering structure factor is

$$\left| F(\vec{H}) \right|^2 = \left| \sum_{\kappa} b_\kappa \exp(-i\vec{H} \cdot \vec{r}_\kappa) \exp(-W_\kappa) \right|^2 ,$$

and the Lorentz factor is

$$G(\theta) = \begin{cases} \lambda^2/\sin\theta & \text{for radial scans} \\ \lambda^2/\cos\theta & \text{for transverse scans.} \end{cases}$$

In this expression $\vec{H}$ is a reciprocal-lattice vector, $\vec{r}_\kappa$ is the position of the κth atom in the unit cell, b_κ is the scattering length, W_κ the Debye-Waller factor, and 2θ the scattering angle for the neutrons. An extinction correction of the form

$$Y(\vec{H}) = [1 + 2gG(\theta)|F(\vec{H})|^2]^{-1}$$

was applied.

Since the phase transition is thought to be characterized by a static ferrorotation of the $OsCl_6$ octahedra, the data below T_c were fitted to a collective model in which the covalently bonded $OsCl_6$ octahedral units were considered to be rigid entities that rotate in phase by an angle $\langle\theta(Cl)\rangle \equiv \theta_{coll}$ from the cubic axes. Due to the cubic symmetry of the crystal, the collective rotation of the octahedra may occur about any of the cubic axes. Consequently, six equally populated domains will be formed on passing through the transition. The contributions from all six domains are summed to give the total intensity from the crystal. For rigid molecules the Debye-Waller factor for the Cl atoms takes the form

$$W_{Cl} = \tfrac{1}{2}[|\vec{H}|^2\langle u^2(OsCl_6)\rangle + |\vec{r}_{Cl} \times \vec{H}|^2\langle\theta^2(Cl)\rangle],$$

where $\langle u^2(OsCl_6)\rangle$ is the mean-square translational displacement of the rigid $OsCl_6$ octahedra and $\langle\theta^2(Cl)\rangle$ is their mean-square librational displacement. The adjustable parameters of the model are as follows: (i) the angle of rotation of the $OsCl_6$ octahedra about the cubic axes $\langle\theta(Cl)\rangle = \theta_{coll}$; (ii) the mean-square librational displacement of the $OsCl_6$ octahedra $\langle\theta^2(Cl)\rangle$; (iii) the mean-square translational displacement of the $OsCl_6$ octahedra $\langle u^2(OsCl_6)\rangle$; (iv) the mean-square translational displacement of the potassium atoms $\langle u^2(K)\rangle$; (v) the chlorine position parameter defined as the Os-Cl bond length in units of the cubic lattice parameter X_{Cl}; (vi) the extinction parameter g; (vii) the fraction of second-order neutrons in the beam $f(\frac{1}{2}\lambda)$; and (viii) a scale factor. The neutron scattering lengths[9] are quoted in Table II.

Above T_c two models were considered to describe the results. One model corresponds to a phase transition that is displacive in nature. The adjustable parameters are as above except that $\langle\theta(Cl)\rangle$ is fixed at zero. The other model is of the order-disorder type in which the octahedra randomly hop between the six equivalent orientations $(\pm\theta_{hop}, 0, 0), (0, \pm\theta_{hop}, 0), (0, 0, \pm\theta_{hop})$. The scattered amplitudes from equal numbers of octahedra in each of the six orientations are summed to give the total scattered amplitude from the crystal. The adjustable parameters are those listed above except that $\langle\theta(Cl)\rangle$ is used to denote θ_{hop}.

The parameters for each model were varied so as to minimize by least squares the quantity

$$Q_2 = \frac{1}{N-M}\sum_{i=1}^{N}(I_i^{obs} - I_i^{calc})^2 W_i ,$$

where N is the number of observed intensities I_i^{obs}, M is the number of adjustable parameters, I_i^{calc} are the calculated intensities and W_i the weights assigned to the individual measurements. As a second measure of the goodness of fit the parameter

$$R = \sum_{i=1}^{N}|F_i^{obs} - F_i^{calc}| \Big/ \sum_{i=1}^{N} F_i^{obs} ,$$

where F_i^{obs} and F_i^{calc} are the observed and calculated structure amplitudes, was evaluated.

A. Low-temperature structure

The final parameters of the least-squares analysis of the 4.6-K data with $W_i = 1/I_i^{obs}$ are given in Table II and the calculated intensities using these best-fit model parameters are compared with the measured intensities in Table I. Several relevant atomic displacements which are derived from the parameters are listed in Table III.

The agreement between the measured intensities and those calculated by the simple model is surprisingly good, bearing in mind that the intensities span a range of three orders of magnitude. The parameters deduced from the analysis are insensitive to the choice of weighting. In particular, the best-fit parameters for a least-squares fit with $W_i = 1/(I_i^{obs})^2$ all agree with those listed in Table II within the quoted errors. The most important parameter from the point of view of the phase transition is the collective rotation angle of the $OsCl_6$ octahedra. The analysis of the 4.6-K data gives $\theta_{coll} = 3.6 \pm 0.2$ deg, in good agreement with the approximate value of 3 deg deduced from NQR data.[10] This rotation angle may be taken as an order parameter to characterize the transition.

It is to be expected that the collective rotation of the $OsCl_6$ octahedra will be accompanied by a small tetragonal distortion of the lattice and by the introduction of anisotropy in the Debye-Waller factors which describe the motions of the octahedra. Therefore, the model was refined to take these effects into account. It was found that the fit to the data was not significantly improved and that the additional parameters to describe the anisotropies were zero within the limits to which they were specified.

Finally, an attempt was made to represent the data using an antiferrorotative model even though satellite reflections were not observed below T_c. In this model some of the $OsCl_6$ octahedra in the unit cell were rotated clockwise and others rotated anticlockwise through an equal angle. The fraction

TABLE III. The Os–Cl bond length and the atomic displacements determined from the parameters of Table II.

Distances (Å)	298 K		4.6 K
	Displacive	Order-disorder	
Displacement of Cl due to collective rotation	0	NA	0.15
Displacement of Cl due to hopping rotation	NA [a]	0.28–0	NA
Root-mean-square displacement of Cl due to libration of $OsCl_6$	0.17	0–0.17	0.07
Root-mean-square displacement of Cl due to translation of $OsCl_6$	0.12	0.12	0.19
Root-mean-square displacement of K	0.20	0.20	0.19
Os–Cl bond length	2.326	2.326	2.332

[a] Not applicable.

of clockwise and anticlockwise rotated octahedra was treated as a variable parameter. When this fraction was fixed at one half, (i.e., equal numbers of clockwise and anticlockwise rotated octahedra) the resulting best fit had an R factor three times larger than that of the ferrorotative models, and several of the observed intensities could not be adequately fitted. When this fraction was allowed to vary, its value for the best fit was found to be unity i.e., a ferrorotative model was chosen as the best fit. This result constitutes further evidence that the phase transition in K_2OsCl_6 is indeed ferrorotative.

B. High-temperature structure

The displacive model provides a good description of the 298-K data. The final parameters of the least-squares analysis with $W_i = 1/I_i^{obs}$ are given in Table II and the calculated intensities using these best-fit model parameters are compared with the normalized measured intensities in Table I. Several relevant atomic displacements which are derived from the parameters are listed in Table III.

The agreement between the measured intensities and those calculated by the model is very good. With one exception the parameters deduced from the analysis are insensitive to the choice of weighting; the best-fit parameter $\langle u^2(OsCl_6)\rangle$ for $W_i = 1/(I_i^{obs})^2$ is smaller by a factor three than that appearing in Table II. A fitting procedure that is thought to be better than least squares and that assigns weights to individual data points in such a way that highly deviant points are given less weight is the robust-resistant technique.[11] When this procedure was applied all the fitted parameters agreed within error with those listed in Table II.

To investigate the validity of a small nonzero value of $\langle\theta(Cl)\rangle$ above T_c, as earlier reported[12] for K_2ReCl_6, the displacive model was fitted to the K_2OsCl_6 data with $\langle\theta(Cl)\rangle$ allowed to vary. The fit that was obtained with $W_i = 1/I_i^{obs}$ gave a small nonzero value of the angle, $\langle\theta(Cl)\rangle \sim 0.9$ deg, but was no better than the fit for $\langle\theta(Cl)\rangle = 0$. For $W_i = 1/(I_i^{obs})^2$, a nonzero angle $\langle\theta(Cl)\rangle \sim 0.9$ deg was also obtained and gave a somewhat better fit than the model with $\langle\theta(Cl)\rangle = 0$. We believe that these results are artifacts of the fitting procedure without physical merit. In support of this conclusion one might note that the rms librational displacement of the octahedra at 298 K is much larger than the apparent nonzero rotation angle.

The order-disorder model provides as good a description of the 298-K data as the displacive model. The fitting procedure indicated a strong correlation between the two parameters $\langle\theta^2(Cl)\rangle$ and $\langle\theta(Cl)\rangle \equiv \theta_{hop}$; the two could not be determined simultaneously. A correlation between these two parameters is not unexpected, since, in their effect on the scattering, the hopping displacements are equivalent, in leading order, to a mean-square librational displacement. One of the parameters was therefore assigned a series of fixed values and the other allowed to vary in the least-squares analysis. In this manner the correlation between θ_{hop} and $\langle\theta^2(Cl)\rangle$ shown in Fig. 1 was established. In the limit $\theta_{hop} = 0$, the parameters deduced from the analysis are, as expected, those given in Table II for the displacive model. All θ_{hop}, $\langle\theta^2(Cl)\rangle$ pairs that satisfy the relation depicted in Fig. 1 result in equally good fits to the data with the other parameters having values that within error agree with those in Table II. It is significant that the collective rotation angle $\theta_{coll} = 3.6$ deg found for the low-temperature phase is contained within the range of possible values of θ_{hop} for the high temperature phase. For $\theta_{hop} = 3.6$ deg, Fig. 1 shows

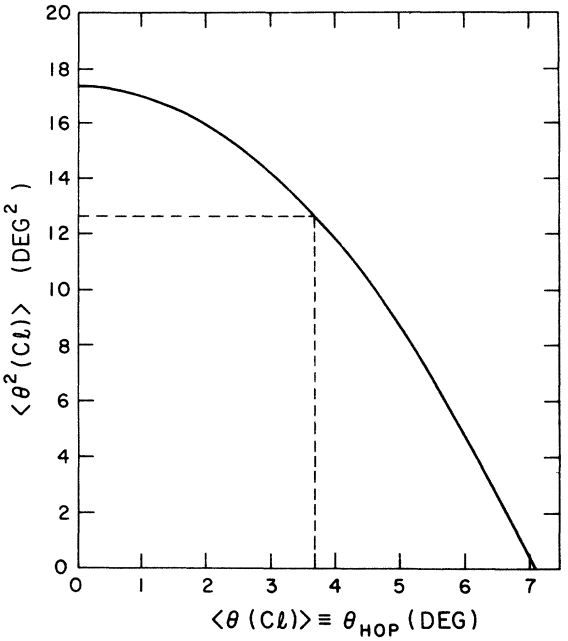

FIG. 1. Correlation between $\langle\theta(\mathrm{Cl})\rangle \equiv \theta_{\mathrm{hop}}$ and $\langle\theta^2(\mathrm{Cl})\rangle$ for the order-disorder model fitted to the 298-K data. The dashed line designates the value of $\langle\theta(\mathrm{Cl})\rangle$ obtained from the low-temperature structure and the corresponding value of $\langle\theta^2(\mathrm{Cl})\rangle$.

that $\langle\theta^2(\mathrm{Cl})\rangle = 13$ deg^2 as compared to $\langle\theta^2(\mathrm{Cl})\rangle = 17$ deg^2 from the displacive model.

From Table III it is seen that the decrease in the value of the chlorine position parameter at 298 K from that observed at 4.6 K combined with the increase in the lattice parameter shows that the Os–Cl bond length remains essentially unchanged with temperature. In addition the change across the phase transition is small for the K atom parameter but is large for the three parameters which define the motion of the rigid octahedra. The magnitudes of the mean-square displacements are larger than expected, particularly for the $OsCl_6$ translation at 4.6 K (that is, they correspond to very low Einstein frequencies). It is interesting to note that mean-square displacements of similar magnitude have been deduced from elastic neutron scattering measurements[13] in K_2SnCl_6.

IV. TEMPERATURE DEPENDENCES OF (117), (337) BRAGG PEAKS NEAR T_c

To investigate the critical properties of the phase transition the temperature dependences of certain Bragg peaks were studied in the vicinity of T_c. The (117) and (337) reflections were chosen because preliminary measurements showed them to exhibit the largest variation with temperature of 25 reflections investigated in the $(\bar{1}10)$ scattering plane. The results shown in Fig. 2 demonstrate that the phase transition in K_2OsCl_6 is continuous.

The Bragg peak intensity at temperatures above T_c is almost independent of temperature. Below T_c the intensity has a component which is assumed in the multidomain specimen to depend on the square of the order parameter θ^2_{coll}, since θ_{coll} is small.[14] Consequently, if the intensity observed above T_c is subtracted from the intensities below T_c, the resulting "reduced intensity" will depend on the square of the order parameter, and thus on the reduced temperature. The dependence will have the form

$$I^{\mathrm{red}} \propto [(T_c - T)/T_c]^{2\beta}.$$

By plotting this dependence on log-log scales for various reasonable choices of T_c (see Fig. 2) a transition temperature of $T_c = 44.5 \pm 0.4$ K was seen to give the best straight line. The results are shown in Fig. 3 for this value of T_c. The values of

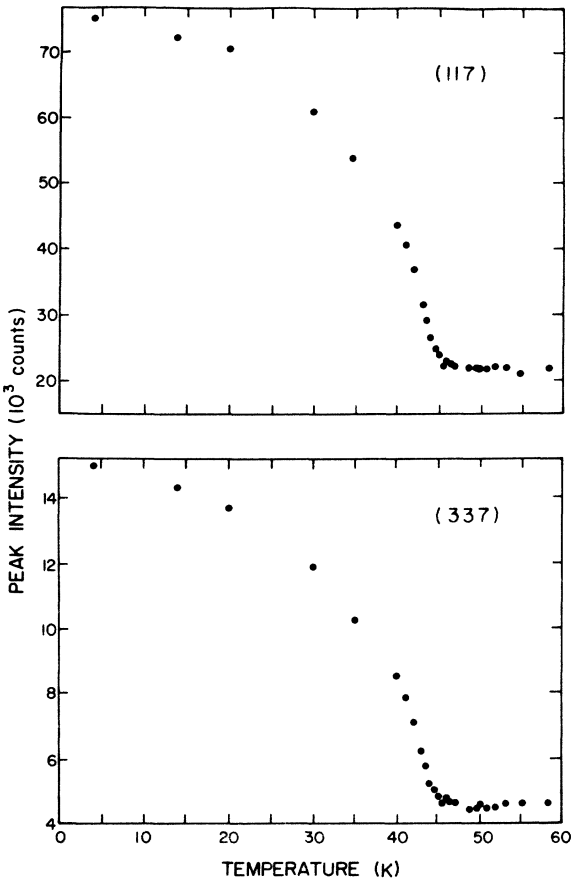

FIG. 2. Temperature dependence of the Bragg peak intensities in K_2OsCl_6 for the two reflections.

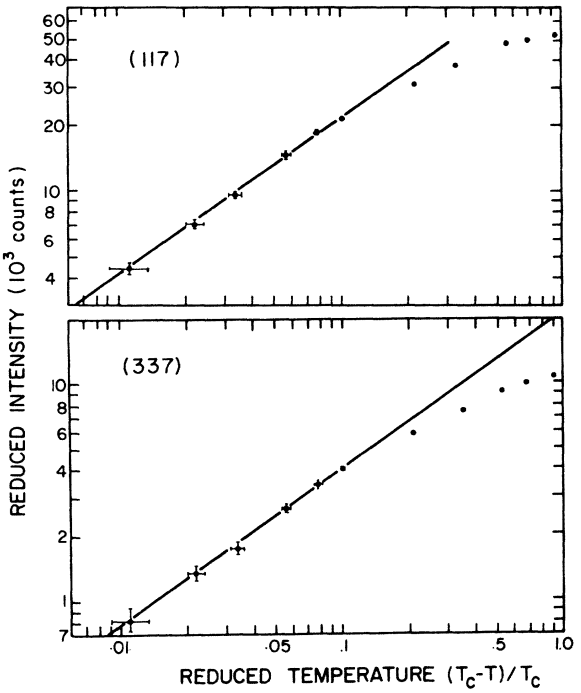

FIG. 3. Reduced intensities vs reduced temperature for the two reflections. A value $T_c = 44.5$ K is used.

β are found to be 0.35 ± 0.06 and 0.36 ± 0.05 from the (337) and (117) data, respectively, in good agreement with the exponent $\beta = 0.31$ of the three-dimensional Ising model.[15]

V. CONCLUSIONS

The structure of K_2OsCl_6 has been measured above and below the phase transition by means of elastic neutron scattering. The change in structure below T_c is characterized by a collective ferrorotation of rigid $OsCl_6$ octahedra. This is the principle conclusion of the present work. The data are consistent with either a displacive or an order-disorder model. Inelastic neutron-scattering experiments are in progress with the intention of measuring the temperature dependence of the rotary lattice modes in the vicinity of T_c. It is hoped that these measurements will give further insight into the nature of the transition and possibly allow a definite choice to be made between the two models. The present work shows that the angle of rotation is the order parameter, and it is observed to change continuously below a T_c of 44.5 K with an exponent typical of three-dimensional phase transitions.

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