Order-Disorder Transitions in the s=1/2 Chromate $(NH_4)_3CrO_8$

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Abstract

We have recently examined the s=1/2 chromate system $(NH_4)_3CrO_8$ with x-ray diffraction experiments. At low temperatures, we discovered that there are two structural transitions. One of these transitions was noted before at 137.5 K, but the other, at ~250 K, has been noted here for the first time. Specific heat measurements confirmed the existence of this second transition. We believe that both of these are order-disorder transitions which involve the orientation of the NH_4 molecules. The anomalous low-temperature specific heat anomaly below 1 K is still a mystery.

X Rays

X-rays were first observed and documented in 1895 by Wilhelm Conrad Roentgen, a German scientist who found them quite by accident when experimenting with vacuum tubes, and called it "X" to indicate it was an unknown type of radiation.

Some of the most important contributions of X-ray technology have been in the world of medicine. X-rays have also played a crucial role in a number of other areas as well like crystallography, by using the diffraction of X-rays.

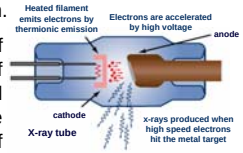


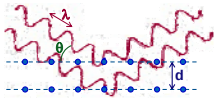
Figure 1: X-ray production

X Ray Diffraction

Max Von Laue proposed in 1912 that a crystal might serve as a kind of three-dimensional diffraction grating for x rays. That is, a beam of x rays might be scattered by the individual atoms in a crystal, and the scattered waves might interfere just like waves from a diffraction grating. By using a crystal as a diffraction grating, von Laue had proved that the X-rays were waves of light with very small wavelengths.

In 1913 W.H. Bragg designed and made an X-ray spectrometer that would allow many types of crystals to be investigated using his son's theory.

$$n\lambda = 2d\sin(\theta)$$



where

- λ is the wavelength of the rays
- θ is the angle between the incident rays and the surface of the crystal
- d is the spacing between layers of atoms

and constructive interference occurs when n is an integer (whole number)

Figure 2: Bragg's Law

By changing the angle of the incident X-rays, W.H. Bragg measured the reflections at different angles from the faces of the crystal. He found that very strong reflections occurred at certain angles. These strong reflections depended on the spacing of the planes of atoms inside the crystal, according to his son Bragg's Law. By measuring all the angles at which strong reflections occurred, the Braggs worked out the arrangement of individual atoms inside the crystals.

The Ammonium Peroxychromate, $(NH_4)_3CrO_8$

Figure 3 depicts the unit cell of $(NH_4)_3CrO_8$, based on x-rays diffraction data according to Harter, Cage, Nguyen, Abboud and Dalal research (2005).

Their magnetic susceptibility measurements fully supported this behavior. Their heat capacity data, on the other hand, exhibited a small but sharp peak at 137.5 K, as shown in Figure 4.

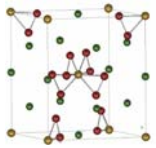


Figure 3: unit cell of $(NH_4)_3CrO_8$

This peak indicated the presence of some form of order-disorder phase transition of the NH_4 molecules.

The low temperature heat capacity feature is still a mystery and believed to be magnetic in origin. NASA is interested in this material as a bolometer for outer space equipment.

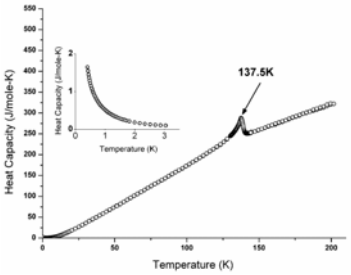


Figure 4: Temperature dependence of heat capacity for $(NH_4)_3CrO_8$

The Experiment

Picture 1: X-Ray diffraction Machine

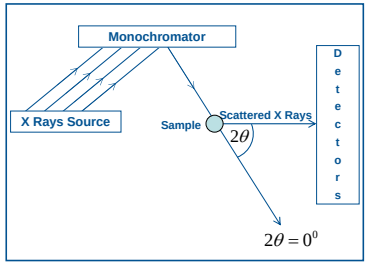


Figure 5: The Measurement

The Experiment's Results

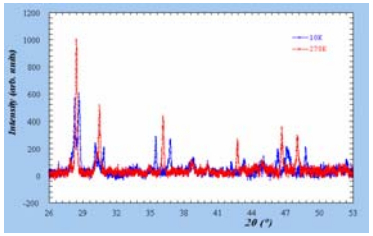


Figure 6: The X-Ray diffraction patterns for temperatures of 10K and 270 K. Notice the peak splitting at low temperatures, indicating a change in structure.

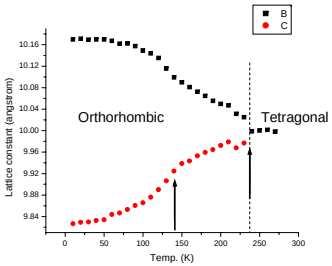


Figure 7: The lattice spacing versus temperature. Note that there are changes in the structure at both transitions in the specific heat.

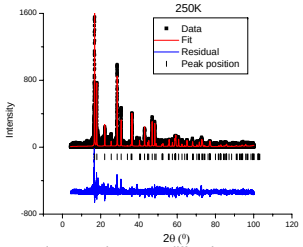


Figure 8: The X-Ray diffraction patterns fitting by using the Rietveld refinement

The Rietveld refinement of the structure can be used to track structural changes as a function of temperature.

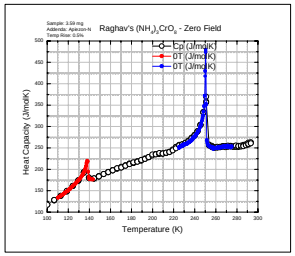


Figure 9: Temperature dependence of heat capacity for $(NH_4)_3CrO_8$ according to our measurements.

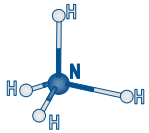


Figure 10: The NH_4 molecules. The transitions are due to reorientations of the NH_4 molecules.

The two structural transitions are seen in the specific heat. If we integrate C/T, we can measure the entropy release at the two transitions, which are 3.464 J/mol K and 3.350 J/mol K. If these are both order-disorder transitions of the NH_4 molecules, then the theoretical entropy release would be $\Delta S = R \cdot \ln 2 = 5.763$ J/mol K.

Conclusions

We have observed two order-disorder transitions in $(NH_4)_3CrO_8$ via x-ray scattering and heat capacity measurements. Both of these transitions are structural in nature. The low-temperature heat capacity anomaly below 1 K must be magnetic in origin, and is the target of future experiments.

Acknowledgements

- Professor Chris Wiebe (mentor)
- Dr. Pat Dixon, Director, CIRL
- Jose Sanchez, Assistant Director, CIRL
- The National Science Foundation
- N. S. Dalal, Department of Chemistry, NHMFL/FSU
- Ragdelv Sament, Department of Chemistry, NHMFL/FSU
- Brain Fairhurst, Assistant Director, Magnet Lab
- Mary Bauman, REU Program
- Dr. Yehuda Jacobson, Manager of Yigal-Alon High School

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