The Production of Sr_2VO_4 for Neutron Scattering Experiment

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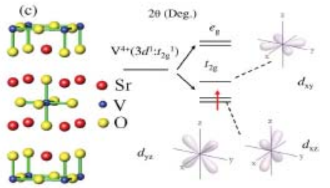
Abstract: The purpose of this experiment is to successfully create an appreciable amount of Strontium Vanadate, Sr_2VO_4, which will be significant enough for use in a neutron scattering experiment at ISIS. We are attempting to gain more knowledge about the orbital ordering transition. Magnetic susceptibility, x-ray diffraction, and heat capacity measurements were completed to investigate the spin ordering at ~ 97 K. Neutron scattering experiments will be completed at the ISIS research center near Oxford, using the HET spectrometer.

Introduction

Strontium Vanadate, or Sr_2VO_4, is an interesting compound in the family of layered perovskites. A perovskite is a class of materials which generally form in a cubic structure and in most often contain oxygen as a major chemical component. Perovskite materials exhibit lot of interesting and intriguing properties both from theoretical point of view as well as in its applications. Some of these are colossal magnetoresistance, charge ordering, spin dependent transport, interplay of structural, as well as magnetic and transport properties. These compounds are used as catalyst electrodes in certain types of fuel cells and are candidates for memory devices and spintronics applications. In this specific case however, we are interested in Sr_2VO_4 because it is similar to La_2CuO_4 , or Lanthanum Cuprate. La_2CuO_4 is a parent compound to high Tc superconductors, and has many correlations with Sr_2VO_4. Both have Spin=1/2 layered magnetic atoms, but the La_2CuO_4 case orders anti-ferromagnetically. Sr_2VO_4 on the other hand, has an unusual orbital ordering. This strange electronic state is not well understood and may be related to the superconductivity in the parent compound. Our developments here may help to shed some light in some of these areas



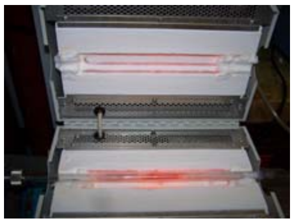
The crystal structure of Sr_2VO_4 and the 3d orbital levels for its V4+ ion.

Experimental Procedure

The Production of Sr_2VO_4 is a two-step reaction, which takes precision and time. The chemical formulae are listed here:

(1) $4\ SrCO_2 + V_2O_5 + \rightarrow Sr_4V_2O_9 + 4\ CO_2$
(2) $Sr_4V_2O_9 + H_2 \rightarrow 2\ Sr_2VO_4 + H_2O$

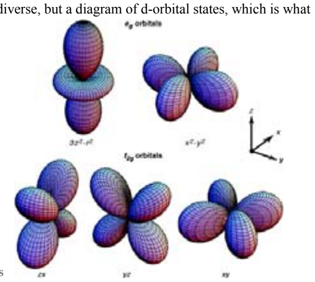
The first step of the reaction, in which $Sr_4V_2O_9$ is produced, is prepared by grinding the Strontium Carbonate and Vanadium Oxide with a mortar and pestle until mixed thoroughly. Then, the mixture is fired at 1073 K for 20 hours. At this point the powder is mixed again and re-fired. After a third time, the sample has been fired for a total of 60 hours and the reaction is finished. The $Sr_4V_2O_9$, a white, chalky powder now, is then distributed along an Alumina half pipe, keeping in mind that surface area is key to a successful reaction as gas will be the other precipitate. The half-pipe of sample is then placed in a tube furnace under Hydrogen flow at 1323 K for 30 hours. At this time, the sample must be ground and an X-Ray is taken. Then the sample is re-fired. After a total of 90 hours, the $Sr_4V_2O_9$ has turned from chalky white to jet black, and the transition to Sr_2VO_4 is complete. There are many factors which play a part in this reaction, and if one of them is out of sync, the sample can be flawed. One of the most important of these factors is temperature. Because the temperature must be so high, only a small amount, about 0.3 grams, can be fired in the tube furnace at once, so that it can be contained in small space surrounding the heating implement of the furnace. This is the only the area of the furnace where the tempereraturе will remain hot enough to induce reaction with the H_2 gas. Needless to say, this procedure had to be conducted several times in order to achieve the desired amount of sample.



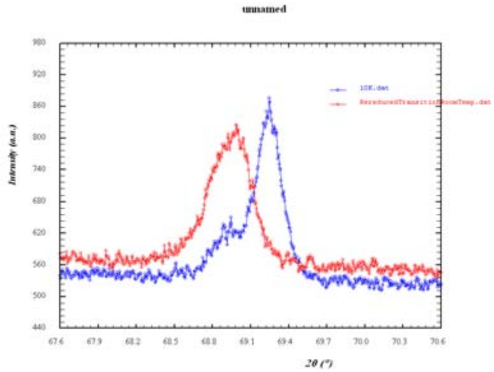
Top Left: Sr_4V2O_9 before it is put into the tube furnace.
Top Right: Sr_2VO_4 just after burning.
Bottom : Sr_2VO_4 in mortar with pestle.

Orbital Physics

There are many words for an orbital: electron configuration, probability cloud, e^- cloud… These all refer to the same thing of course, and it all goes back to quantum mechanics. Quantum physics states that it is not possible to know the precise position of an electron at any given time, as it would violate the Heisenberg uncertainty principle. On the other hand, we know that there is an explicitly defined probability that it is occupying at a certain point. An orbital is nothing more than that set of points which the electron is likely to occupy. Complicated physics dictates the different orders of configuration, and they are many and diverse, but a diagram of d-orbital states, which is what we are concerned with here, is given below. In the case of Strontium Vanadate there is an interesting orbital transition at ~97 K. It turns out that there is an actual phase separation here, which is typical in many orbitally ordered systems such as this one. Low-temperature x-ray diffraction Experiments were completed to investigate this orbital-ordering transition in Sr_2VO_4. Below 122 K, several Bragg peaks broaden in Q and become split. In particular, the (200) peak can be fit to two Lorentzians in the temperature range between 122 and 94 K. Below 94 K, this peak can be fit to only one Lorentzian. This can have two possible origins: (i) there are two coexisting tetragonal phases between 122 and 94 K, or (ii) an orthorhombic phase must exist between 122 and 94 K, which evolves into a different tetragonal phase below 94 K. [1]



Right: Common D-orbitals

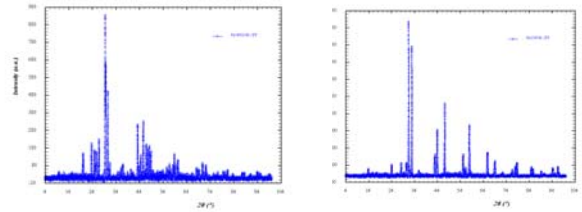


This is an excerpt of an X-Ray diffraction pattern illustrating the structural change in Sr_2VO_4 at low temperatures (red lines – 10 K, blue lines – room temperature). Note the broadening of the Bragg peak.

X-Ray Diffraction and HUBER

Diffraction occurs as waves interact with a regular structure whose repeat distance is about the same as the wavelength. The phenomenon is common in the natural world, and occurs across a broad range of scales. For example, light can be diffracted by a grating having scribed lines spaced on the order of a few thousand angstroms, about the wavelength of light. It happens that x-rays have wavelengths on the order of a few angstroms, the same as typical interatomic distances in crystalline solids. Using x-ray diffraction, the structure of atomic compounds can be studied and categorized. For all of the experiments conducted here were recorded by a HUBER imaging plate Guinier camera 670 using Cu $K\alpha1$ radiation (1.54059Å) with a Ge monochromator. Data were collected in steps of 0.005 with temperatures down to 9 K obtained with a closed cycle He fridge.

HUBER imaging plate Guinier camera 670, which was used for the x-ray diffraction experiments



These are X-Ray diffraction patterns of $Sr_4V_2O_9$ and Sr_2VO_4 (left to right)

Neutron Diffraction Experiment at ISIS

In September, the final portion of this experiment will be conducted using the HET Spectrometer at ISIS, a research facility located in England. The HET is essentially a powerful neutron detector which is optimized for collecting large quantities of neutrons at high energies. Hopefully, this experiment will allow us to see the orbital ordering through the neutron spin interaction with the unpaired electrons in the Vanadium of $Sr_4V_2O_9$, and we be able to measure the energy difference between the d-orbitals. The detector will measure the speed of neutrons as they leave the sample, which can be used to determine whether energy has been lost or gained. If the neutron becomes excited and induces a spin to a higher level, it loses energy, whereas if a spin falls to a lower level, energy is gained. At the orbital ordering transition, the spectrum in our sample should change. As we record more and more scattering events, we can map out the different energy levels. This is similar to the process of mapping out atomic levels using light as a probe.

ISIS, the world's leading pulsed neutron & muon source situated at the Rutherford Appleton Laboratory near Oxford, UK.

Conclusion

This experiment was a success. We have created a sufficient amount of Strontium Vanadate, which will be used in the upcoming neutron scattering experiment this September. Approximately 2.6 grams of Sr_2VO_4 has been synthesized. To the knowledge of this research team, this is the largest amount of Strontium Vanadate amassed since its discovery. X-ray diffraction measurements were taken, and they illustrated the structural change of the orbitals in Sr_2VO_4 at ~97 Kelvin, inducing phase separation at that point.

Acknowledgements

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References

[1] H. D. Zhou, B. S. Conner, L. Balicas, C. R. Wiebe, *Orbital Ordering in Sr_2VO_4*, Physical Review Letters (2007).

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