ESRF	**Experiment title:** Structural Investigation of the New Inorganic Spin-Peierls NaV_2O_5	**Experiment number:** HS396
Beamline: ID15A	**Date of Experiment:** from: 9.9.97 to: 12.9.97	**Date of Report:** March, 1998
Shifts: 12	**Local contact(s):** K.D. Liß	Received at ESRF: 17 MAR. 1998

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Report:

Since the discovery of high temperature superconductivity in doped antiferromagnetic cuprate materials there has been a renewed interest in low dimensional quantum antiferromagnets. A linear S = 1/2 chain with antiferromagnetic interaction along the chain interacting with the three-dimensional phonons can lead to a spin-Peierls (SP) phase transition. A dimerization of the spin chain below the transition temperature T_{SP} leads to the formation of a non-magnetic singlet ground state. The transition is called a spin-Peierls transition because it is a magnetic analog of a Peierls transition in quasi-one-dimensional conductors. This transition was initially observed only in a few organic compounds. The discovery of a SP-state in the inorganic compound $CuGeO_3$ [1] has renewed strong interest in this phenomenon. Recently Isobe and Ueda [2] have discovered a new inorganic spin-Peierls system α'-NaV_2O_5. Magnetic susceptibility measurements on both polycrystalline samples [2] and single crystals [3] have shown that a spin gap opens below $T_{SP} \approx 34$ K and Raman scattering measurements [3] show a crystallographic distortion below T_{SP}. Thus α'-NaV_2O_5 seems to be a spin-Peierls compound with the highest critical temperature so far known T_{SP} = 34 K. Here we report the results of our synchrotron X-ray diffraction investigations on a single crystal of α'-NaV_2O_5.

Single crystals of α'-NaV_2O_5 were grown by a self-flux method. A single crystal of dimensions of about 6 x 0.6 x 0.1 mm^3 was mounted inside the helium cryostat of the triple-axis diffractometer of the high energy beam line ID15 of the European Synchrotron Radiation Facility. The X-ray wavelength was 0.105 Å which corresponds to the X-ray energy of 114.3 keV. We detected superlattice reflections below $T_{SP} \approx 34$ K corresponding to the cell doubling along a and b and quadrupling along c. We measured the intensities of several main and superlattice reflections. The superlattice reflections are relatively strong in the X-ray experiment being of the order of about 10^{-1} of the main reflections. Fig. 1 shows the temperature variation of the integrated intensity of the $\frac{3}{2}\frac{1}{2}\frac{15}{4}$ superlattice reflection. The intensity

of this reflection decreases continuously and becomes zero at $T_{SP} \approx 34$ K showing that the phase transition is of the second order. We have measured thermal expansion anomaly due to the magnetoelastic effects close to the spin-Peierls transition temperature. Fig. 2 shows the temperature variation of $\frac{\Delta d}{d}$ for the 005 reflection. For systems without any phase transition one expects the $\frac{\Delta d}{d}$ value to attain the zero value at very low temperature. In the present case however the $\frac{\Delta d}{d}$ value decreases with decreasing temperature but then starts increasing continuously at T_{SP}. We interpret this abrupt increase in the $\frac{\Delta d}{d}$ value due to the magnetoelastic coupling. The results of the present synchrotron X-ray diffraction study together with similar neutron diffraction investigations performed at the four-circle triple-axis diffractometer of the ILL on the same single crystal allow us to reach a very important conclusion about the structural modulation of α'-NaV_2O_5 below T_{SP}. The very fact that the intensities of the superlattice reflections in the X-ray diffraction experiment are of the order of 10^{-1} those of the main reflections whereas in the neutron diffraction the corresponding ratio is of the order of 10^{-4} implies that the structural modulation below T_{SP} is essentially due to vanadium atoms. A possible model for the low temperature structure can be obtained by "decorating" the zig-zag vanadium chains parallel to the crystallographic b axis. The doubling of the b axis can be easily achieved by modulating the V-V distance (short S and long L). In the high temperature phase they are equal (D) along the zig-zag chain. So if one has the sequence S-L-L-L-S-L.. . in the low temperature phase instead of the sequence D-D-D-D-D.. . at room temperature then the unit cell is doubled along b. If we also decorate the next parallel chains as we move along the a axis like L-S-L-L-L-S.. . , L-L-S-L-L-L-S. . . and L-L-L-S-L-L-L-S... we get cell doubling along the a axis. Now it is easy to stack these chains in the a-b plane along c in order to get the cell quadrupling along the c axis, although there are several ways of doing this. Such a model has indeed given a reasonable fit to the low temperature X-ray diffraction data which are limited to one reciprocal layer.

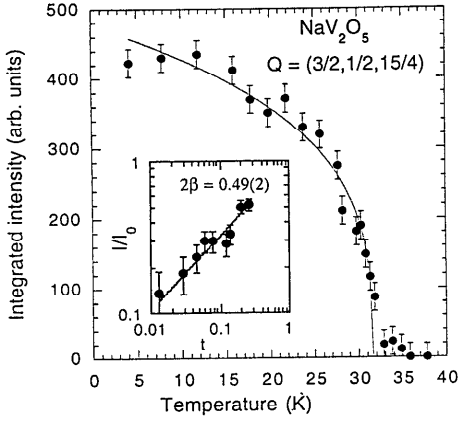

Fig. 1 - Temperature variation of the integrated intensity of the $\frac{3}{2}\frac{1}{2}\frac{15}{4}$ superlattice reflection.

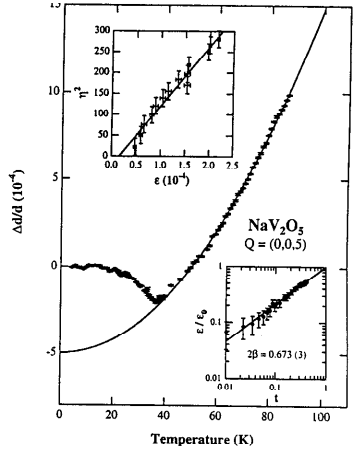

Fig. 2 - Temperature variation of $\frac{\Delta d}{d}$ for the 005 reflection.

References

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