

PII: S0038–1098(98)00305-6

THE GROUND STATE OF NaV₂O₅Tapan Chatterji,^a K.D. Liß,^b G.J. McIntyre,^a M. Weiden,^{c,d} R. Hauptmann^c and C. Geibel^{c,d}^aInstitut Laue-Langevin, BP 156, F-38042 Grenoble Cedex 9, France^bEuropean Synchrotron Radiation Facility, Grenoble, France^cTechnische Physik, Technische Hochschule Darmstadt, Germany^dMax-Planck-Institut für CPfS, Dresden, Germany

(Received 5 June 1998; accepted 15 June 1998 by P. Burlet)

Neutron and X-ray diffraction experiments have shown that NaV₂O₅ consists of zig-zag V chains of average valence 4.5 rather than a charge ordered state at room temperature. Both these experiments revealed superlattice reflections below the phase transition temperature $T_{SP} \approx 34$ K. The modulation below T_{SP} is due to displacements predominantly of V atoms for which we propose a model. © 1998 Elsevier Science Ltd. All rights reserved

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 [1–3]. The transition is called a spin-Peierls transition because it is the magnetic analog of the Peierls transition in quasi-one-dimensional conductors. The SP transition was initially observed only in a few organic compounds [4]. The discovery of a SP-state in the inorganic compound CuGeO₃ [5] has renewed strong interest in this phenomenon. Recently Isobe and Ueda [6] discovered a new inorganic spin-Peierls system NaV₂O₅. Magnetic susceptibility measurements on both polycrystalline samples [6] and single crystals [7] have shown that a spin gap opens below $T_{SP} \approx 34$ K and Raman scattering measurements [7] imply a crystallographic distortion below T_{SP} . Low-temperature X-ray diffraction measurements [8] on single crystals showed superlattice reflections with a lattice modulation vector $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{4})$. Also inelastic neutron scattering [8] from a powder sample showed an energy gap of $\Delta = 9.8$ meV at a scattering vector $\mathbf{Q} = 1.0 \text{ \AA}^{-1}$ corresponding to the reciprocal lattice point $(1, \frac{1}{2}, 0)$. Thus NaV₂O₅ seems to be a spin-Peierls compound with the highest critical temperature so far known $T_{SP} = 34$ K.

However, for NaV₂O₅ $2\Delta/k_B T_{SP} \approx 6.44$ which is almost double the value of 3.53 expected from a BCS-type theory in the weak coupling limit. All other known organic and inorganic spin-Peierls systems have $2\Delta/k_B T_{SP}$ close to the expected BCS value. According to [9] NaV₂O₅ crystallizes in the non-centrosymmetric orthorhombic space group $P2_1mn$ with lattice parameters $a = 11.318 \pm 0.005$, $b = 3.611 \pm 0.002$, $c = 4.979 \pm 0.003 \text{ \AA}$ at room temperature. The non-centrosymmetric structure allows two independent V atoms in the unit cell. This led to the belief [6–9] that the crystal structure contains V⁴⁺ ($S = 1/2$)-chains along the b -axis, in which spins are antiferromagnetically coupled. These chains are separated from each other by non-magnetic V⁵⁺-chains, which results in a quasi-one-dimensional behaviour along the V⁴⁺ chains. To our knowledge there exists no experimental evidence of such a charge-ordered state which is on the contrary incompatible with the recent Raman scattering experiments [10]. In this letter we show that NaV₂O₅ is not a conventional spin-Peierls system with $S = 1/2$ linear chains but consists of zig-zag chains of V atoms with average valence of 4.5 above T_{SP} . Based on our neutron and synchrotron X-ray diffraction data below T_{SP} we propose a model for the low temperature structure of NaV₂O₅.

Single crystals of NaV₂O₅ were grown by a self-flux method. A single crystal of dimensions of about $6 \times 0.6 \times 0.1 \text{ mm}^3$ was mounted inside the 4-circle cryostat of the diffractometer D10 of the Institut Laue-Langevin. We measured the intensities of the hkl and $hk-l$

reflections at 295 K yielding 346 unique reflections at a neutron wavelength of 1.26 Å. Least-squares refinements of the structure models against these data and also room temperature X-ray diffraction data obtained from laboratory X-ray diffractometer were performed in both the centrosymmetric ($Pm\bar{m}n$) and the non-centrosymmetric ($P2_1mn$) space groups. A comparison of the results of these two refinements led us to conclude that the actual space group of NaV_2O_5 is the centrosymmetric $Pm\bar{m}n$. Details of the structural analysis will be published elsewhere [11]. There is thus only one symmetry independent V atom in the unit cell and to describe the structure as having magnetic V^{4+} chains separated by non-magnetic V^{5+} -chains along the b axis is not correct, at least not at room temperature. Instead one should consider zig-zag chains of crystallographically indistinguishable V ions with an average valence of 4.5. Thus V atoms in NaV_2O_5 are most probably in an insulating mixed-valent state at room temperature. 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 at 5 K by using a neutron wavelength of 2.36 Å. The superlattice reflections are very weak being of the order of about 10^{-4} of the main reflections. Figure 1 shows scans of the $\frac{3}{2} \frac{1}{2} \frac{11}{4}$ superlattice reflection measured by neutrons at several temperatures. The intensity of this reflection increases continuously below $T_{SP} \approx 34$ K and saturates at low temperatures.

X-ray synchrotron measurements were performed on the same single crystal as used in the neutron diffraction experiment on the high-energy beam line ID15A of the European Synchrotron Radiation Facility. The X-ray wavelength was 0.105 Å which corresponds to an X-ray energy of 114.3 keV. A search for superlattice reflections at 4.2 K again revealed intensities corresponding to the cell doubling along a and b and quadrupling along c . Figure 2 shows the temperature variation of the intensity of the $\frac{3}{2} \frac{1}{2} \frac{15}{4}$ superlattice reflection. The intensity decreases continuously and becomes zero at $T_{SP} \approx 34$ K. The continuous variation of the intensity of the reflection shows that the spin-Peierls transition is of the second order. The result is in agreement with those of Fujii *et al.* [9]. We determined the intensities of a number of superlattice and main reflections at 4.2 K. The ratio of the intensity of superlattice to the main reflections in the X-ray data is of the order of 0.1.

We also measured using synchrotron X-ray diffraction the thermal expansion anomaly due to the magnetoelastic effects close to the spin-Peierls transition temperature. Figure 3 shows the temperature variation of $\Delta d/d$ for the 005 reflection. For systems without any

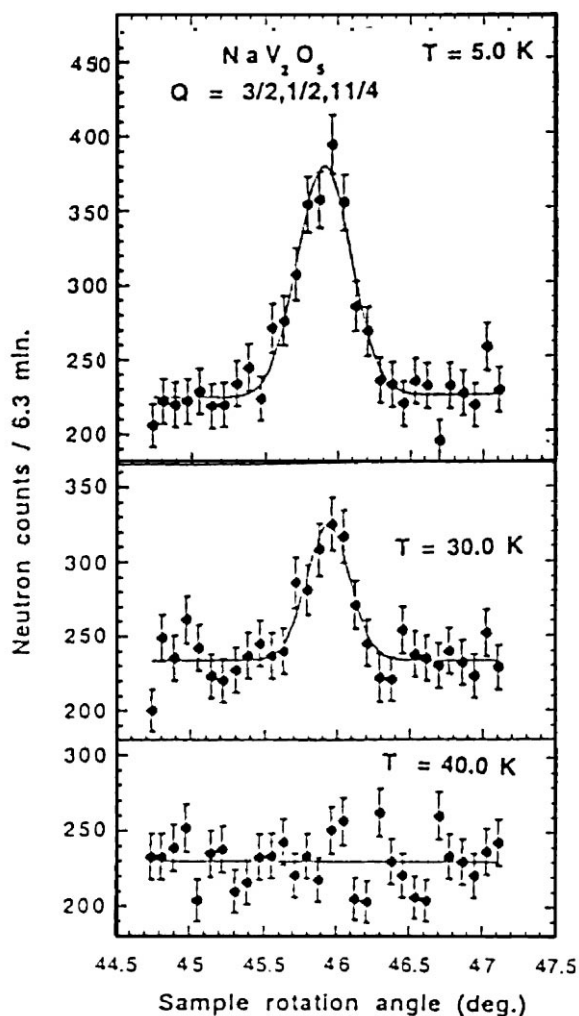


Fig. 1. Coupled $\omega - x\theta$ scans of the $\frac{3}{2} \frac{1}{2} \frac{11}{4}$ superlattice reflection of NaV_2O_5 measured by neutron diffraction at several temperatures.

phase transition one expects the $\Delta d/d$ value to attain a constant value at very low temperatures. In the presence case however the $\Delta d/d$ value decreases with decreasing temperature but then starts increasing continuously at T_{SP} . We interpret this abrupt increase in the $\Delta d/d$ value to be due to the magnetoelastic coupling. By extrapolating the $\Delta d/d$ values and then subtracting we have separated the strain $\epsilon = \Delta d/d$ due to the magnetoelastic effects from the phonon contribution. The inset on the bottom right of Fig. 3 shows the log-log plot of normalized strain ϵ/ϵ_0 against reduced temperature t in the critical regime. According to the phenomenological Landau theory the spontaneous strains can be treated by a coupling between the elastic strain ϵ_i and the order parameter η of the phase transition which is the lattice distortion connected with the dimerization of the V ions. This adds a term $\mu_i \epsilon_i \eta^2$ to the free energy, where μ_i s denote the coupling constants. Considering in addition

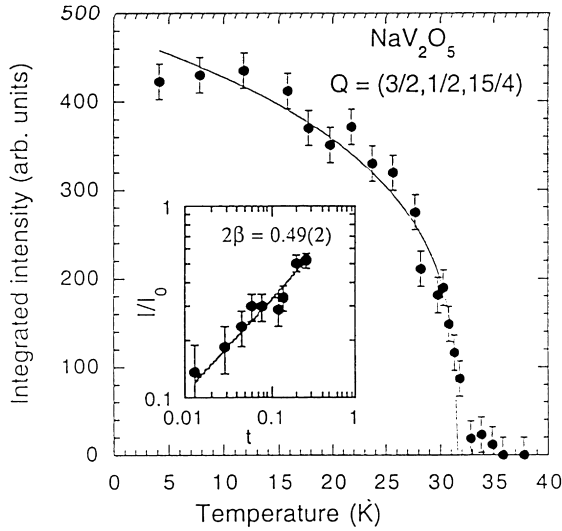


Fig. 2. Temperature variation of the intensity of the $\frac{3}{2} \frac{1}{2} \frac{15}{4}$ superlattice reflection of NaV_2O_5 measured by synchrotron X-ray diffraction. The inset shows the log–log plot of the reduced intensity vs the reduced temperature $t = T_{SP} - T/T_{SP}$.

the elastic energy of the lattice $C\epsilon^2$ (C is the elastic constant) and the condition of the stress free system, $\partial F/\partial \epsilon_i = 0$, one obtains the spontaneous strains to be proportional to the square of the order parameter, i.e. $\epsilon(T) \propto \eta^2(T)$. The inset on the left top of Fig. 3 shows a plot of $\epsilon = \Delta d/d$ at different temperatures below T_{SP} against the integrated intensity of the $\frac{3}{2} \frac{1}{2} \frac{15}{4}$ reflection which is the square of the order parameter η^2 . The linear plot shows that the strain is approximately proportional to the square of the order parameter. The slope of the log–log plot of the reduced strain ϵ/ϵ_0 vs the reduced temperature t shown the bottom right inset of Fig. 3 gives $2\beta = 0.673 \pm 0.003$ ($\beta = 0.336 \pm 0.02$). It is not quite obvious why the thermal expansion anomaly along c (perpendicular to the V chain) should be rather large, but it may be connected to anharmonic thermal motion of the O atoms along the c axis below T_{SP} . Our results agree well with the thermal expansion investigations [12] by capacitance dilatometric technique.

The results of the present joint X-ray and neutron diffraction study allow us to reach a very important conclusion about the structural modulation of 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. The neutron scattering length of V is only $-0.0382(1) \times 10^{-12}$ cm, whereas those of Na and O are $0.363(2) \times 10^{-12}$ and $0.5805(4) \times 10^{-12}$ cm,

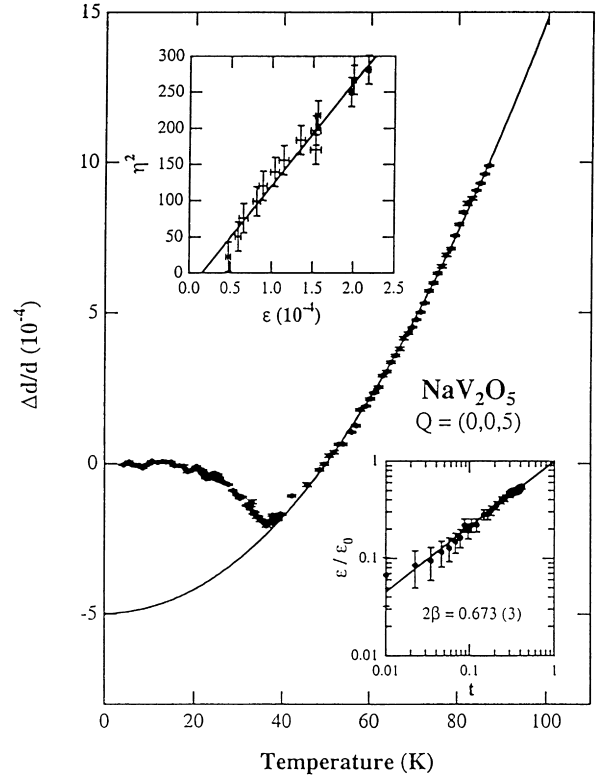


Fig. 3. Temperature variation of the relative change in lattice spacing $\Delta d/d$ of NaV_2O_5 along $[0\ 0\ 5]$. The inset at bottom right shows the log–log plot of normalized strain ϵ/ϵ_0 against reduced temperature t in the critical regime. The inset at top left shows a plot of $\Delta d/d$ (strain) along $[0\ 0\ 5]$ at different temperatures below T_{SP} against the integrated intensity of the $\frac{3}{2} \frac{1}{2} \frac{15}{4}$ superlattice reflection which is proportional the square of the order parameter.

respectively. The X-ray atomic scattering factors in the forward direction for V, Na and O are 23, 11 and 8 electrons, respectively. Thus the V atoms contribute very strongly to the X-ray intensities but very weakly to the neutron intensities. Indeed for this reason we were able to refine neutron diffraction intensity data of only the main reflections from both polycrystalline and single crystals of NaV_2O_5 collected at 4.2 K with parameters essentially of the high temperature structure. 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, S being the distance between the d^1 dimers). 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 successive parallel chains as we move along the a axis as L-S-L-L-L-S...,

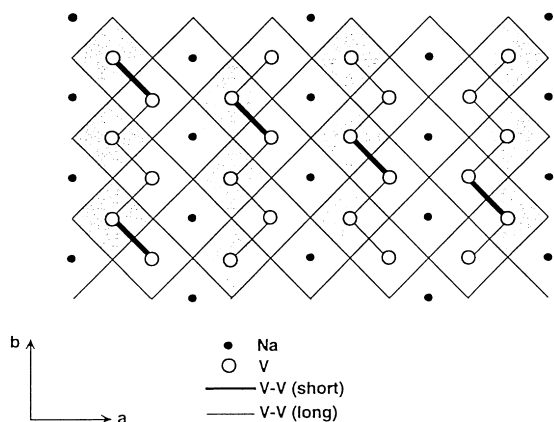


Fig. 4. Schematic representation of a possible model of the low-temperature modulated structure of NaV_2O_5 projected on to the a - b plane.

L-L-S-L-L-L-S... and L-L-L-S-L-L-L-S... we get cell doubling along the a axis (see Fig. 4). 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. One such a model has indeed given a reasonable fit to the low temperature X-ray diffraction data which are limited to one reciprocal layer [14]. It is to be noted that similar V-V pair (short distance S) was invoked by Chakraverty *et al.* [13] in vanadium bronze $\text{Na}_{0.33}\text{V}_2\text{O}_5$.

In conclusion our structural investigations have shown that the belief [6–9] that NaV_2O_5 consists of distinguishable magnetic V^{4+} chains separated by non-magnetic V^{5+} chains is not correct, at least not at room temperature. The structure consists of zig-zag chains of indistinguishable V ions of average valency of 4.5. So instead of considering a half-filled single chain and an empty parallel chain, one should consider the same number of electrons in the zig-zag chain, i.e. an extended (significant overlap) Hubbard model that is quarter filled. It is not quite clear whether such a system can have a

spin-Peierls-like ground state or not. The high value of T_{SP} and the large $2\Delta/k_B T_{SP}$ of NaV_2O_5 compared to other conventional spin-Peierls systems may be connected to this. Based on our joint neutron and synchrotron X-ray diffraction data we have proposed a possible model for the low temperature structure of NaV_2O_5 which can be termed as a “valence- or bond-density-wave”. Fluctuations can reduce the transition temperature in such chains leading to a larger $2\Delta/k_B T_{SP}$ as observed experimentally. Additionally we have shown the existence of large thermal expansion anomaly below T_{SP} along c which is perpendicular to the V chain direction.

Acknowledgements—We wish to thank Professor H.G. von Schnering, Dr. B.K. Chakraverty, Dr. T. Ziman and Dr. P. Thalmeier for critical discussion.

REFERENCES

1. Bulaevskii, L.N., *Soviet Phys. – Solid State*, **11**, 1969, 921.
2. Cross, M.C., *Phys. Rev.*, **B20**, 1979, 4606.
3. Pytte, E., *Phys. Rev.*, **B10**, 1974, 4637.
4. Bray, J.W. *et al.*, *Phys. Rev. Lett.*, **35**, 1975, 744.
5. Hase, M. *et al.*, *Phys. Rev. Lett.*, **70**, 1993, 3651.
6. Isobe, M. and Ueda, Y., *Phys. Soc. Jap.*, **65**, 1996, 1178.
7. Weiden, M. *et al.*, *Z. Phys.*, **B103**, 1997, 1.
8. Fujii, Y. *et al.*, *J. Phys. Soc. Japan*, **66**, 1997, 326.
9. Carpy, A. and Galy, J., *Acta Cryst.*, **B31**, 1975, 1481.
10. Fischer, M. *et al.* (to be published).
11. Chatterji, T. *et al.* (to be published); von Schnering, H.G. *et al.*, *Z. Krist.*, **213**, 1998, 246.
12. Köppen, M. *et al.* (to be published).
13. Chakraverty, B.K. *et al.*, *Phys. Rev.*, **B17**, 1978, 3781.
14. Chatterji, T., von Schnering, H.G. and Grin, Y. (to be published). The model given in Fig. 4 was originally suggested by Professor H.G. von Schnering after the modulation vector of the low temperature phase was determined.