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Knight Shift Measurements Through the NiAs–MnP Structure Change in Vanadium Monosulfide*

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Knight-shift data have been obtained for a series of nonstoichiometric VS_x phases with the MnP and NiAs structure types. The data demonstrate that the change in symmetry is accompanied by an abrupt change in the Knight shift indicating that the symmetry change is accompanied by a change in the character of the conduction electrons.

Introduction

Vanadium monosulfide with the NiAs structure type has been known since the work of Biltz and Köcher in 1939 (*1*). In 1963 it was reported that there also exists a vanadium monosulfide with the MnP structure type. The MnP-type structure can be viewed as a distortion of the NiAs-type structure, as can be seen in Fig. 1. Figure 1 shows a projection of the atom positions onto the 010 plane of the orthorhombic unit cell. When the atoms are located in the positions indicated by the circles the space group symmetry is $P6_3/mmc$ and the structure type is NiAs. When the atom positions are displaced from the NiAs positions as indicated by the arrows the space group symmetry is *Pcmn* and the structure type is MnP (*2*).

The possibility of a continuous distortion of the crystal structure from the NiAs-type to the MnP-type was considered in an investigation of the variation of the lattice parameters of non-stoichiometric vanadium monosulfide as a function of composition (*3*). This study revealed an unusual behavior of the room temperature orthorhombic *a* and *b* parameters which is summarized in Fig. 2.

It was concluded that the distortion of the NiAs structure occurs in a nearly continuous fashion with increasing V/S starting at V/S = 0.94, as indicated in Fig. 2. Discontinuous changes in

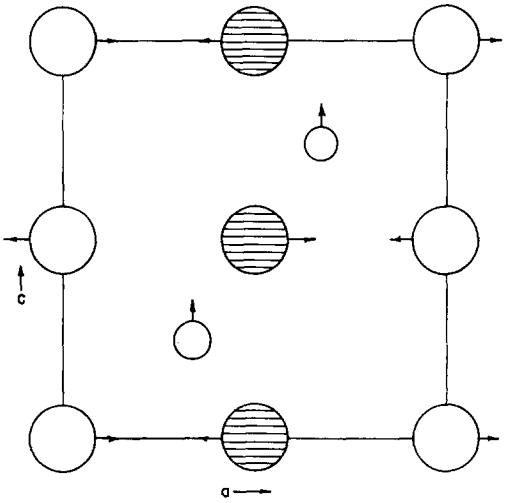

FIG. 1. Projection of the NiAs structure of $VS_{1.06}$ onto the 010 plane of the orthorhombic unit cell. The arrows indicate the directions of movement to produce the MnP structure type. The large circles represent metal atoms at $y = 0$ and $y = \frac{1}{2}$ (shaded).

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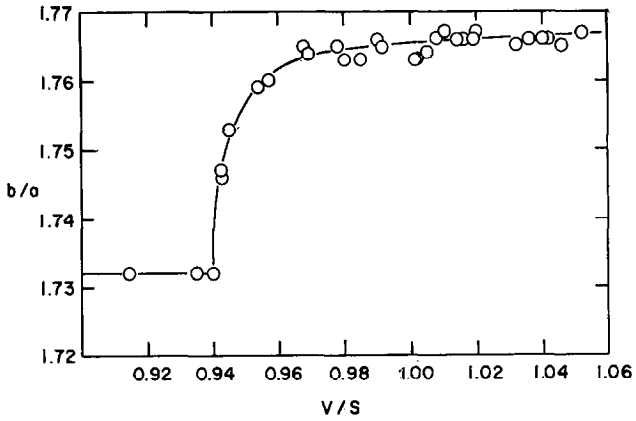

FIG. 2. Room temperature b/a values for nonstoichiometric vanadium monosulfide vs vanadium/sulfur ratios as reported by Franzen and Burger (*3*).

symmetry that occur with continuous changes in composition are frequently associated with order-disorder phenomena. However the NiAs–type to MnP–type transition is a displacive transition and it is not associated with ordering of defects. Nor is the transition associated with a change in defect type since the density data of Ref. 3 indicated that in the range $0.90 < V/S < 1.00$ the vanadium monosulfide phase is nonstoichiometric due principally (>98%) to the presence of vanadium vacancies and that the concentration of vacancies at random vanadium positions decreases continuously through the transition point as V/S increases.

Vanadium monosulfide was reported to exhibit anomalies in its susceptibility and specific heat with changing temperature at about 900°K (*4*). The anomalies were thought to accompany antiferromagnetic ordering, however neutron diffraction measurements (*5*) at room temperature failed to provide evidence of magnetic ordering in $VS_{1.0}$ with the MnP-type structure. Therefore, it seems likely that the observed magnetic and specific heat anomalies were associated with the NiAs to MnP symmetry change in a vanadium monosulfide sample. The magnetic susceptibilities of the VS sample were observed (*4*) to be on the order of those expected for Pauli paramagnetism (3×10^{-6} emu g^{-1} at room temperature).

Experimental

Samples of vanadium monosulfide were prepared in three steps: 1. initial combination of the elements in fused silica tubes at temperatures of about 500°C, 2. intermediate annealing at 850°C in sealed tantalum tubes, and 3. final annealing at 1350–1400°C in tungsten crucibles. The starting materials were high purity (>99.99% pure) elements. The resultant samples were identified by comparison of the lattice parameters obtained using the Guinier X-ray diffraction technique with those reported in Ref. 3.

Knight shift data were collected at frequencies of, 4.5, 13, 20, and 26 MHz using a spectrometer designed by D. R. Torgeson (*6*) and the method of continuous averaging. The vanadium Knight shifts were measured relative to the ^{51}V effective gyromagnetic ratio of 1.11927 MHz/kOe using ^{27}Al in an $AlCl_3$ solution as an intermediate reference. The ratio $\nu(v)/\nu(Al) = 1.0089$.

Results

The NMR line widths were observed to vary linearly with applied field. The Knights shifts were extrapolated to zero frequency to eliminate the effects of the random vacancies. The extrapolated Knight shifts are shown plotted versus the V/S ratio in Fig. 3.

Discussion

Because of the variety of factors affecting the Knight shift (Fermi contact, core polarization, field induced orbital moments) it is not possible to give a detailed interpretation of the decrease in Knight shift which accompanies the transition. However, the qualitative fact that the symmetry change is accompanied by a change in the Knight shift does permit the conclusion that the sym-

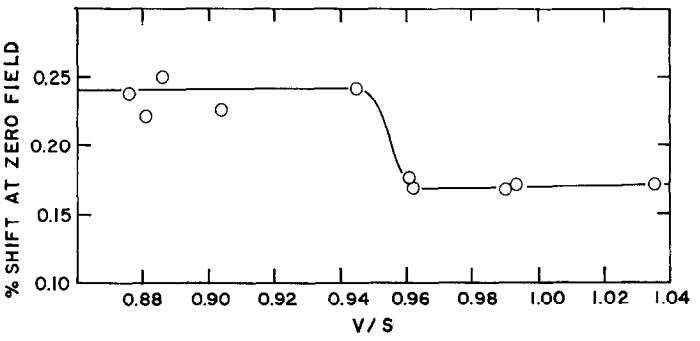

FIG. 3. Percent shift at zero field vs V/S.

metry change occurs together with a change in the nature or extent of the interaction of the conduction electrons with the vanadium nuclear spins. This conclusion in turn suggests a change in the contribution of orbitals centered on the vanadium atoms to the conduction band at the Fermi energy.

An interpretation of the symmetry change in terms of electron concentration effects would be consistent with a number of facts known about the NiAs and MnP structures. For example, TiS and VP (both with 10 valence electrons per formula unit) have the NiAs-type structure, whereas $VS_{1.00}$ and CrP (both with 11 valence electrons per formula unit) both have the MnP-type structure. Also, a NiAs–MnP symmetry change has been observed in (Ti, Cr) As and (Ti, V) As with increasing Cr/Ti and V/Ti, respectively (*7*). The continuous distortion in $V_{1-x}S$ would be accompanied by the continuous filling of states in the band, and would be associated with a single valued Knight shift. For no sample was a shift characteristic of the NiAs-type structure (~0.17%) and also a shift characteristic of the MnP-type structure (~0.24%) observed indicating that a two-phase region is narrower than $\Delta(V/S) = 0.02$, the separation of the V/S values of the most vanadium-rich hexagonal phase and the most sulfur-rich orthorhombic phase investigated.

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