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On The Magnetic Anomaly in $Mn_{0.25}NbS_2$

The ordered superlattice phases in $Mn_{0.25}NbS_2$ have been studied as a function of temperature by electron diffraction. It is found that one phase becomes disordered at 688°K ± 20°K. It is suggested that this structural change is responsible for the magnetic anomaly previously reported to occur in these crystals at about 680°K.

It is well known that a wide variety of transition metals can be introduced between the layers of NbS_2 and TaS_2 to form ternary intercalation compounds (*1*, *2*). Several workers (*3–5*) have studied compounds of the type M_xNbS_2 (M = Mn, Fe, Co, Ni) by X-ray diffraction and shown that for $x = 0.25$ and $x = 0.33$ the intercalate atoms form superstructures of the 2H–NbS_2 host crystal lattice. Rouxel *et al.* (*6*) studied these compounds over a wide range of x and showed that, although a rhombohedral polytype occurred for very small values of x, the 2H–NbS_2 structure was observed for x in the range from 0.1 to 0.5. These compounds have unusual magnetic properties which have been studied by several workers (*5–7*). In 1971 van Laar *et al.* (*8*) reported a study of the magnetic properties of the intercalated transition metal dichalcogenides M_xNbS_2 and M_xTaS_2 (M = transition metal). These authors observed anomalies in the magnetic susceptibility versus temperature curves for $Mn_{0.25}NbS_2$ and $Mn_{0.25}TaS_2$ at 680 and 690°K, respectively. The latter crystals were examined by neutron diffraction at room temperature and 725°K but no structural change was detected; however, X-ray diffraction at high temperature showed a discontinuous change in the c_0 parameter of both crystals at the transition point. They suggested that the transition was correlated with a change in the Mn–Nb interaction.

In the course of electron diffraction studies on the ordering of intercalated atoms in layered crystals, we have recently studied ordering in $Fe_{0.25}NbS_2$ and noted an abrupt change in the ordered arrangement at about 650°K (*9*). In fact, in these crystals there are two ordered phases present at room temperature; one phase has a $2a_0$ periodicity and the second phase has a $3^{1/2}a_0$ periodicity (a_0 is the unit cell edge length of NbS_2). In slowly cooled specimens the $2a_0$ phase accounts for most of the volume, although the spots corresponding to the $3^{1/2}a_0$ are easily detected in the electron diffraction patterns. At about 650°K the $2a_0$ phase suddenly becomes disordered and simultaneously hexagonal lines of diffuse scattering appear. At this, or a somewhat higher temperature, the intensities of the $3^{1/2}a_0$ diffraction spots gradually increase.

Since it was expected that Mn would behave in a similar manner to Fe in these crystals, it appeared that a similar $2a_0$ superlattice transition in $Mn_{0.25}NbS_2$ might account for the magnetic anomaly noted above. Single crystals of this material were prepared by sealing weighed quantities of the elements in an evacuated quartz tube 1 cm in diameter and about 15 cm long. Five milligrams of iodine per cubic centimeter was added as a transport agent. Crystals were grown over a period of several days in a two-zone furnace with the hot zone at 1290°K and the growth zone at 1140°K. Cleaved, thin specimens of the crystals were examined in the electron microscope. All of the features noted above for $Fe_{0.25}NbS_2$ were also observed in $Mn_{0.25}NbS_2$ diffraction patterns.

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There was some difficulty in establishing the exact temperature at which the $2a_0$ phase disordered during heating in the electron microscope, since the actual specimen temperature is always higher than that indicated by the heating holder thermocouple. Further, there was variation of $\pm 12°K$ in the thermocouple temperature at which the transition occurred in different crystals. It is possible that these variations are due to small composition differences but it is more likely that they are associated with the variable effect of the electron beam which depends both on crystal thickness and thermal contact between the crystal and the grid. It is also possible that the Coulomb interaction between the intercalate ions and the electron beam causes the transition to occur at a somewhat lower temperature than would otherwise be observed. In the case of $Fe_{0.25}NbS_2$ we were able to determine the transition temperature by quenching, from elevated temperatures, crystals sealed in quartz ampoules. This method was not satisfactory for $Mn_{0.25}NbS_2$ since the $2a_0$ phase formed so rapidly that it was not possible to prevent its growth during the quench. Thus we could only infer the transition temperature in $Mn_{0.25}NbS_2$ by assuming that the difference between the "apparent" temperature indicated by the thermocouple and the true temperature was the same as that found for $Fe_{0.25}NbS_2$. On this basis we determined the $2a_0$ transition temperature in $Mn_{0.25}NbS_2$ to be $688 \pm 20°K$. We conclude that this transition is associated with the magnetic anomaly observed at 680°K.

Although these NbS_2 intercalates will decompose at sufficiently high temperatures under vacuum, we note that there was no evidence of decomposition in the electron microscope in the vicinity of the transition temperature even though some specimens were held there for periods up to 30 min. In fact, at the beam currents used, the temperature could be raised about 100°K above the transition point before any decomposition could be detected. Further, the transition was reversible in the electron microscope. For $Mn_{0.25}NbS_2$, if the temperature was reduced about 10°K below the transition point, the diffraction spots corresponding to the $2a_0$ phase were immediately detected. This contrasts with the case of $Fe_{0.25}NbS_2$ where a temperature drop of about 100°K below the transition temperature was required before the $2a_0$ phase nucleated. We believe the rapid nucleation of the $2a_0$ phase in $Mn_{0.25}NbS_2$ is the reason we were unsuccessful in retaining the high-temperature phase by quenching. Some of the $Mn_{0.25}NbS_2$ speciments were cycled back and forth through the transition many times without any detectable change in the transition temperature. When specimens were cooled from the transition point to room temperature and reheated there was no change in their behavior.

The $3^{1/2}a_0$ phase was not detected in $Mn_{0.25}NbS_2$ by van Laar *et al.* (*8*) probably due to the relatively weak diffraction effects. However, these authors did note that in the $2a_0$ phase continuous linear chains Mn–Nb–Mn–Nb ––– exist parallel to the *c*-axis, while in the $3^{1/2}a_0$ phase at the composition $x = 0.33$ the Mn atoms are located in isolated Nb–Mn–Nb groups. In fact, we believe that, as in $Fe_{0.25}NbS_2$ (*9*), the crowding of the metal atoms along the continuous chains causes the $2a_0$ phase to become unstable at elevated temperatures and the Mn ions take on the same arrangement as at the composition $x = 0.33$ but with one quarter of the Mn atoms missing so that the actual composition is $x = 0.33 - 0.08 = 0.25$. This rearrangement may also account for the discontinuous change observed in c_0 at the transition temperature (*8*).

In a recent review of the magnetic properties of the transition metal layered dichalcogenides Vandenberg–Voorhoeve (*2* has noted that Verhoeven (*10*) found anomalies in the magnetic susceptibles of $M_{0.25}NbSe_2$ (M = Ti, V, Cr, Mn, Ni) at about 750°K and suggested that these may possibly be related to a disordering of the intercalated atoms. In view of

the structural similarity of NbS_2 and $NbSe_2$ it appears likely that rearrangements of the intercalated atoms in the selenides, similar to those described above, are responsible for the magnetic anomalies.

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