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Stoichiometry, Structure, and Physical Properties of Niobium Disulfide[1]

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Samples with stoichiometries near NbS_2 have been prepared from the elements by reaction at 950 °C followed by quenching from an annealing temperature of 750 °C. Stoichiometry of the product depends on the pressure of excess sulfur during annealing. In the range $0 < x < 0.18$ for $Nb_{1+x}S_2$ only two phases are observed, a stoichiometric line phase corresponding to the 2H polytype NbS_2 and a nonstoichiometric phase corresponding to 3R-$Nb_{1+x}S_2$. For $0.07 < x < 0.18$, only the 3R polytype is obtained. Superconducting transition temperatures, determined by Meissner flux expulsion, indicate that 2H-NbS_2 superconducts with a transition temperature of 6.3 K. 3R-$Nb_{1+x}S_2$ does not superconduct above 1.7 K. Static magnetic susceptibilities were measured by the Faraday method over the range 4.2–300 K. The susceptibilities of the 3R materials are temperature independent and are of a magnitude and sign characteristic of a Pauli metal. The susceptibility of 2H-NbS_2 is about twice as great and shows a slight linear increase as the temperature is decreased. The magnetic susceptibilities provide no evidence for or against the existence of a charge-density wave. Using a correlation between crystallographic c/a ratio and CDW distortion temperature as observed in other dichalcogenides, we found that the phase limit of 3R-$Nb_{1+x}S_2$ occurs just at the c/a ratio where a distortion should occur at finite temperature. Partially substituted vanadium materials have also been prepared. The first 1% V drops the superconducting transition temperature by 1 K; the T_c is then nearly constant with increasing vanadium content to at least 4.4% V. The vanadium appears to behave throughout as a Curie paramagnet having a d^1 configuration.

Introduction

The layered transition-metal dichalcogenides have been the subject of many recent studies. Structures and properties as of 1969 have been reviewed by Wilson and Yoffe.[2] Electronic properties were more recently reviewed by Yoffe.[3,4] Lieth and Terhell,[5] Balchin,[6] and Lêvy[7] have summarized preparation and crystal growth procedures, and Hulliger[8] has compiled extensive structural information. Phase transitions and charge-density waves were considered by Williams.[9] Gamble and Geballe[10] and Whittingham[11] have reviewed the chemistry of intercalation.

The basic structural feature of the layered dichalcogenides is a sandwich composed of one sheet of metal atoms M interposed between two hexagonal-packed sheets of chalcogen atoms X. The coordination of X about M is either trigonal prismatic or distorted octahedral. Various polytypes arise from stacking sandwiches with different metal-atom coordination or with different layer-to-layer registry. The three most common polytypes are shown in Figure 1. In the 1T polytype, the local symmetry is approximately octahedral; in the 2H and 3R, it is trigonal prismatic.

Table I. Reported Lattice Parameters for the 3R Polytype of Niobium Disulfide

a axis, Å	c axis, Å	stated compn	single-layer c/a ratio	ref
3.33	17.80	NbS_2	1.782	*a*
3.33	17.81	NbS_2	1.783	*b*
3.33	17.80–17.85	$Nb_{1+x}S_2$, $0.12 < x < 0.25$	1.782–1.787	*b*
3.33	17.89	$Nb_{1.12}S_2$	1.791	*c*
3.31	17.90	NbS_2	1.803	*d*
3.3303	17.918	NbS_2	1.793	*e*

[a] G. Hagg and N. Schönberg, *Ark. Kemi*, 7, 371 (1954). [b] F. Jellinek, G. Brauer, and H. Müller, *Nature (London)*, **185**, 376 (1960). [c] F. Kadjik and F. Jellinek, *J. Less-Common Met.*, **19**, 421 (1969). [d] F. J. DiSalvo, Ph.D. Thesis, Stanford University, 1971. [e] B. Morosin, *Acta Crystallogr., Sect. B,* **30**, 551 (1974).

Four phases of niobium disulfide have been reported.[12] They are stoichiometric 2H-NbS_2 and 3R-NbS_2 and nonstoichiometric 2H-$Nb_{1+x}S_2$ and 3R-$Nb_{1+x}S_2$. The nonstoichiometry is believed to be accommodated by excess niobium atoms in the gap between adjacent sandwiches. Reported properties are in great dispute. As an example, Table I shows lattice parameters reported for the 3R polytype. Although the a axis is relatively constant, the c axis appears to be growing with time! Similar confusion exists in the electric properties. Superconductivity was first reported by van Maaren and Schaeffer.[13] For a three-layer stoichiometric material, they reported a transition temperature of 5.0–5.5 K, and for a two-layer stoichiometric material, they reported 5.8–6.2 K. They attributed the transition widths to the presence of $Nb_{1+x}S_2$ phases. Single crystals of 2H-NbS_2, claimed to be stoichiometric to within 1%, had a superconducting transition range of 6.1–6.3 K. Various other groups have since reported transition temperatures of 2H- and 3R-NbS_2 ranging from 5.0 to 6.3 K. In light of the apparent problems with nonstoichiometry and identification of polytype, it is surprising that the transition temperatures vary over only 1.3 K.

As part of a larger program to study chemical control of superconductivity, particularly the influence of nonstoichiometry on superconducting transition temperatures, this investigation was undertaken: (1) to determine the conditions under which samples of niobium disulfide with known stoichiometries and structures could be prepared, (2) to determine how

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(1) This research was sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant No. 74-2583 and was supported in part by the National Science Foundation and the Materials Science Center at Cornell University. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation hereon.
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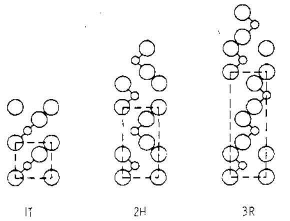

Figure 1. Hexagonal (11$\bar{2}$0) sections of layered compounds MX_2. Small circles represent metal atoms; large circles, chalcogens. Dashed lines outline hexagonal unit cells.

stoichiometry and structure affect the superconducting transition temperature, and (3) to determine whether there is a charge-density wave (periodic lattice distortion) in these materials and whether it is perhaps destroyed by deviation from stoichiometry.

The experimental program consisted of synthesizing a range of niobium disulfides from ultrapure starting materials under carefully controlled conditions, characterizing the composition and structure of the products by chemical and X-ray analysis, measuring the magnetic susceptibility by the Faraday method down to liquid-helium temperatures, and determining the superconducting critical temperatures by flux-expulsion techniques.

In the course of the investigation, it was found that the phase limit of the 3R polytype occurs just at the composition where a charge-density wave (CDW) is expected to occur at finite temperature. To test the hypothesis that it is an incipient CDW which drives the 3R-to-2H phase change, we also prepared vanadium-doped materials. The preparation and properties of these vanadium-substituted niobium disulfides are also described in this report.

Experimental Section

Materials Preparation. Starting materials were niobium wire (Materials Research Corp. "MARZ" grade), niobium foil (Materials Research Corp. or A. D. Mackay), vanadium wire (Materials Research Corp.), and sulfur (Atomergic 99.9999%). The metals were cleaned in concentrated HCl and deionized distilled water. Weighed amounts of the elements were heated together in sealed silica tubes evacuated to less than 10^{-5} torr.

The tubes were slowly heated to 950 °C, allowed to react at 950 °C for about 1 week, cooled at 5 °C/h to the quench temperature, annealed there, and then quenched into cold water. The reaction temperature of 950 °C was chosen on the basis of the following observations: The reaction was extremely slow at 600 °C, and the product, identified by its fibrous or needlelike habit, was primarily NbS_3. At 800 °C unreacted niobium metal was still present after 1 week, and the product gave a diffuse X-ray pattern indicative of inhomogeneity and poor crystallinity. After 1 week at 950 °C, the product was a homogeneous, crystalline material. Reaction for longer than 1 week at 950 °C had no effect on the structure or stoichiometry of the product.

Without annealing, all the samples had unreacted sulfur present in the sample tube. To reduce the amount of unreacted sulfur, we investigated various anneal times and temperatures. Materials annealed at 500 °C contained NbS_3, whereas samples annealed at 750 °C or higher never contained trisulfide. At 750 °C, anneal times longer than a few hours had no effect on the structure or stoichiometry of the product. Thus, reaction for 1 week at 950 °C, cooling at 5 °C/h to 750 °C, and annealing for 1 or 2 days at 750 °C were sufficient to produce samples at equilibrium.

When the sample tubes, which were wrapped in Kanthal wire coils, were quenched in cold water, all the sulfur vapor condensed on the inside walls of the tubes, neatly separating the unreacted sulfur from the niobium sulfide product. Sample tubes were opened in air, and only that portion of a sample which could be easily shaken out of a tube was removed and used for subsequent measurements.

Single crystals were grown by chemical-vapor transport with iodine. Niobium, sulfur, and iodine were weighed into the tubes as described above and the materials heated in multizone tube furnaces with appropriate temperature profiles.

Vanadium-doped samples were shaken to mix the contents after the initial heating. They were then reheated, and the process was repeated. Finally, they were removed from the tube, ground, resealed in new tubes, and reheated.

Analysis of Stoichiometry. The composition of the niobium sulfides was determined by oxidation in air at 800 °C to Nb_2O_5. Niobium was determined by weight of Nb_2O_5 obtained, and sulfur, by difference. The method was checked by oxidation of pure niobium under the same conditions. Values of x in $Nb_{1+x}S_2$ determined for three samples of each material usually agreed to well within ±0.01.

Vanadium-doped samples were analyzed for vanadium content by neutron activation analysis.

Sulfur-Pressure Determination. The pressure of the unreacted sulfur at the quench temperature was determined by comparing the weight of unreacted sulfur per unit tube volume with published tables of sulfur pressure as a function of sulfur density.[14] From the stoichiometry of the product and weight of niobium placed in the tube, the weight of sulfur which had combined with the niobium was obtained. The difference between this and the weight of sulfur initially placed in the tube gave the weight of unreacted sulfur. The internal volume of the tube was determined from its displaced volume, total mass, and density of silica. The volume of the sample itself was small enough to be neglected.

X-ray Analysis. Debye–Scherrer powder diffraction patterns were obtained with a 114.6-mm diameter camera, using copper Kα radiation. Line positions were corrected for film shrinkage and variations in camera diameter by the Straumanis method. Lines were indexed by comparing their positions and intensities with those calculated by using atomic scattering factors given by Moore,[15] and atomic positions, by Jellinek, Brauer, and Müller.[12] The number of layers in the unit cell was determined by comparing the line positions with those calculated by using the powder pattern intensity computer program. The specific polytype was chosen by comparison of calculated and observed line intensities.

Rhombodedral and trigonal materials were indexed in a hexagonal setting. After the indexing, lattice parameters were calculated by Cohen's least-squares method using about 10 lines in the back-reflection region. Only those lines were used which did not overlap or cross other lines as parameters were changed, i.e., those for which there could be no ambiguity in assigning Miller indices.

Some X-ray pictures were taken by using single crystals and a Gandolfi single-crystal randomizer. This device fits into a standard Debye–Scherrer camera and allows the powder pattern of a single crystal to be obtained by randomizing its position with respect to the incoming X-ray beam. In this way, the polytype of a specific single crystal could be determined.

Measurement of Superconducting Transition Temperatures. Superconducting transition temperatures were measured by a standard ac mutual inductance technique. The apparatus was patterned on that described by DiSalvo[16] except that there was no provision for ^{3}He, which simplified the design. Details of the construction are described elsewhere.[17] Samples were contained in small gelatin capsules in one of a pair of nulled secondary coils, coaxially wound with a primary coil. Flux expulsion from the sample on passage into the superconducting state gave an imbalance signal which was amplified by a lock-in amplifer and displayed on the y axis of an X-Y recorder. Simultaneously, the voltage output of a CryoCal resistance thermometer was displayed on the x axis. The critical temperature was taken as the midpoint of the diamagnetic susceptibility rise as temperature was decreased through the transition.

Magnetic Susceptibility. Static magnetic susceptibilities were measured over the range 4.2–300 K by using the Faraday method with Spectrosil quartz buckets and Cahn electrobalance force recording as previously described.[18] The temperature was monitored by vapor pressure of helium, copper/constantan or gold–iron/chromel thermocouples, or a CryoCal resistance thermometer. Susceptibility measurements, which were field independent, were corrected for the diamagnetism of the quartz bucket and are believed to be accurate within 1%.

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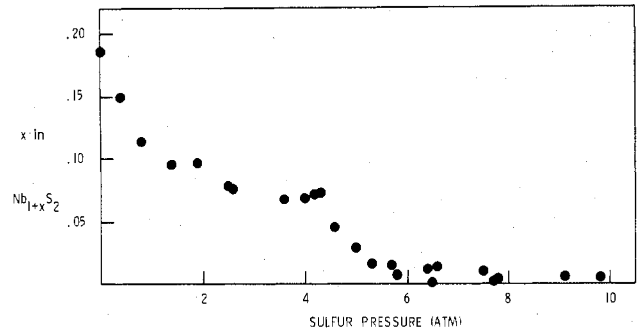

Figure 2. Stoichiometry vs. sulfur pressure for niobium sulfide samples quenched from 750 °C.

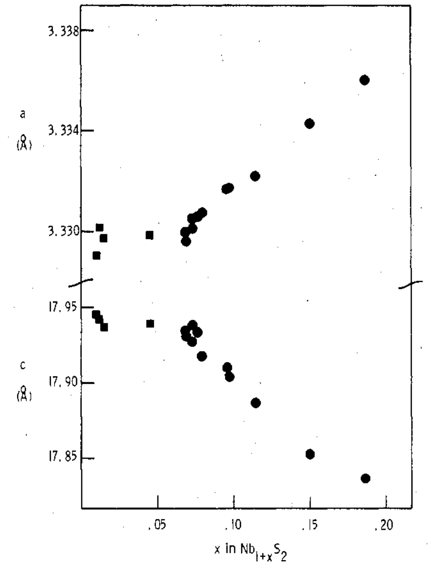

Figure 3. a and c lattice constants of 3R-$Nb_{1+x}S_2$ vs. composition. Circles correspond to 3R polytype alone; squares, to 3R component of 2H–3R mixture.

Results

The stoichiometry of the product niobium disulfide was found to depend on the pressure of excess sulfur in the reaction tube. The results are plotted in Figure 2, for samples quenched from 750 °C. Beginning at the lowest sulfur pressure, x in $Nb_{1+x}S_2$ falls at a decreasing rate with increasing pressure until it levels off finally at an x value very close to 0 for 6 atm and higher pressures. A pressure dependence of this nature indicates two phases are being formed. The phase formed at low sulfur pressure has a phase limit at $x = 0.07$. A few samples were also made at 1000 °C. The shape of the composition vs. temperature curve was qualitatively the same, but all the compositions were shifted to higher sulfur pressures.

At low sulfur pressures, corresponding to $x \geq 0.07$, the X-ray diffraction patterns were those of a pure 3R polytype. The line positions changed with x, yet they remained sharp from sample to sample, indicating that the phase is nonstoichiometric but each sample is a homogeneous material. At higher sulfur pressures, for x very close to 0, only the 2H polytype was observed. At intermediate pressures, $0.07 > x > 0$, the materials contained both 2H and 3R polytypes; the amount of 3R decreased and 2H increased as x decreased to 0.

The hexagonal a and c lattice parameters of 3R-$Nb_{1+x}S_2$ are given as functions of composition in Figure 3. As stoichiometry is approached, the a axis shortens and the c axis lengthens. For x less than 0.07, the a and c lattice parameters are constant, confirming that the sulfur-rich phase limit of 3R-$Nb_{1+x}S_2$ is at $x = 0.07$.

Table II. Superconducting Transition Temperatures of Niobium Sulfides

x in $Nb_{1+x}S_2$	T range, K	T_c, K
0.001	6.25–6.41	6.33
0.005	6.30–6.48	6.39
0.007	6.13–6.32	6.23
0.010	6.03–6.32	6.18
0.012	5.94–6.30	6.12
0.014	6.17–6.33	6.25
0.016	6.16–6.41	6.29
0.029	5.88–6.19	6.04
0.073, pure 3R		<1.7
2H single crystals	6.14–6.32	6.23

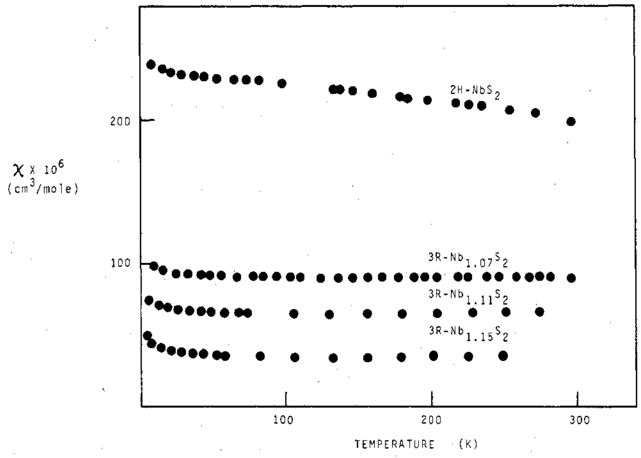

Figure 4. Molar magnetic susceptibilities of niobium sulfides, uncorrected for core diamagnetism.

The lattice parameters of 2H-NbS_2 were more difficult to determine, as many of the X-ray lines are broad, indicating disorder. In spite of the broadened X-ray lines the lattice parameters were determined to be $a = 3.324 \pm 0.003$ Å and $c = 11.95 \pm 0.02$ Å. These values, the average of 11 different samples, were independent of both the sulfur pressure and bulk stoichiometry, as expected for a line phase.

The superconducting transition temperatures of 10 niobium sulfide samples are listed in Table II. Except for the last sample, which consisted of several large single crystals prepared by vapor transport, these were all polycrystalline materials. Superconductivity was observed only in those samples which contained 2H-NbS_2. Signal strength appeared to be proportional to the amount of the 2H polytype present. The transition temperatures are independent of x so long as 2H material is present. No superconducting transition was exhibited by 3R-$Nb_{1+x}S_2$ alone.

Figure 4 shows the static magnetic susceptibilities observed for three 3R-$Nb_{1+x}S_2$ samples and for 2H-NbS_2 as functions of temperature from 4.2 to 300 K. The susceptibilities of the 3R materials are temperature independent and are of a magnitude and sign characteristic of a Pauli metal. The smallness of the "Curie tail" at the lowest temperatures indicates a high degree of purity. The susceptibility of 2H-NbS_2 is high and has a slight temperature dependence; χ increases nearly linearly as the temperature is decreased.

Vanadium-doped materials were made with enough excess sulfur to produce 8 atm at the 750 °C quench temperature. From Figure 2, this would seem to be sufficient to ensure that stoichiometric NbS_2 was formed. When the doped materials were made, however, many of the tubes exploded from excess pressure, especially when the vanadium concentration was high. Apparently the product is metal rich, so that the sulfur pressure is higher than expected. This could result if the vanadium went chiefly into interlayer rather than intralayer sites. Formally, the doped materials can be regarded as $V_yNb_{1-x}V_xS_2$, where

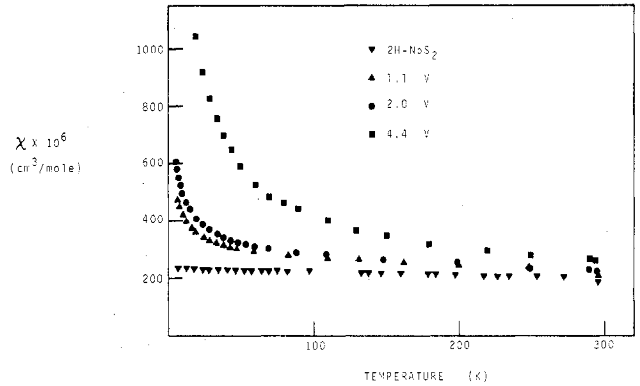

Figure 5. Molar magnetic susceptibilities of vanadium-doped niobium disulfides, uncorrected for core diamagnetism.

x vanadium atoms substitute on niobium sites and y vanadium atoms go between the layers. All the vanadium-doped samples prepared turned out to be the 2H polytype.

Superconducting critical temperatures of the vanadium-doped materials were as follows: 5.14–5.38 K for 1.1% V, 5.24–5.52 K for 1.4% V, 5.05–5.48 K for 2.0% V, and 4.59–5.43 K for 4.4% V. The first 1.1% of V seems to drop the transition temperature from 6.3 to 5.3 K. The transition temperature then remains essentially constant to at least the 4.4% V doping level. Figure 5 shows how the static magnetic susceptibility changes with increased vanadium content. The most striking aspect is the development of a pronounced "Curie tail" at low temperatures. At high temperatures, the susceptibilities tend to that of 2H-NbS_2. Representing the total susceptibility by

$$\chi = \chi_0 + C/(T - \Theta)$$

and approximating the temperature-independent part, χ_0, by observed susceptibility of 2H-NbS_2, we can find the moment responsible for the temperature-dependent part by plotting $(\chi - \chi_0)^{-1}$ vs. T, as is done in Figure 6. Extrapolation of the low-temperature portions leads to the same value, −7 K, for the Weiss constant Θ of each. Using the slopes to get a Curie constant C and assigning it all to vanadium, we find effective magnetic moments per vanadium of 1.6 μ_B in 1.1% V, 1.4 μ_B in 2.0% V, and 1.9 μ_B in 4.4% V. These moments are consistent with a d^1 system.

Discussion

The stoichiometric 3R polytype, 3R-NbS_2, reported previously[12] was not seen in this study. Jellinek[19] has suggested that in addition to thermodynamic factors, the kinetics of crystal growth and solid-state rearrangement control the product obtained. However, no stoichiometric material was ever obtained in this work by any thermal treatment of a one-metal-to-two-sulfur mixture. In addition the lattice constants determined for nonstoichiometric 3R-$Nb_{1+x}S_2$ in this work (compare Table I and Figure 3) span those reported for "stoichiometric" 3R-NbS_2. Thus, it appears that all these materials are nonstoichiometric.

There are several errors that previous investigators may have made in interpreting their data. First, when sample tubes are cooled slowly, as overnight in a furnace, unreacted sulfur may distribute itself throughout the tube. The apparent stoichiometry would then be sulfur rich if the sample and all unreacted sulfur were not separated. Second, impurities might determine both the stoichiometry and polytype obtained from a reaction. The niobium used in this work had a total impurity content of about 250 ppm (which was mostly tantalum), so the sulfides studied here are probably as pure as any studied previously. Finally, even a small amount of the 3R polytype mixed in with the 2H polytype shows up strongly in powder X-ray diffraction patterns, because the diffraction lines of the 3R are much sharper than those of the 2H. A mixture of this type when analyzed would be very close to NbS_2. It would also be a superconductor. So, it would be possible to see superconductivity in a material which was analyzed to be very close to NbS_2 yet had the powder diffraction pattern of the 3R polytype.

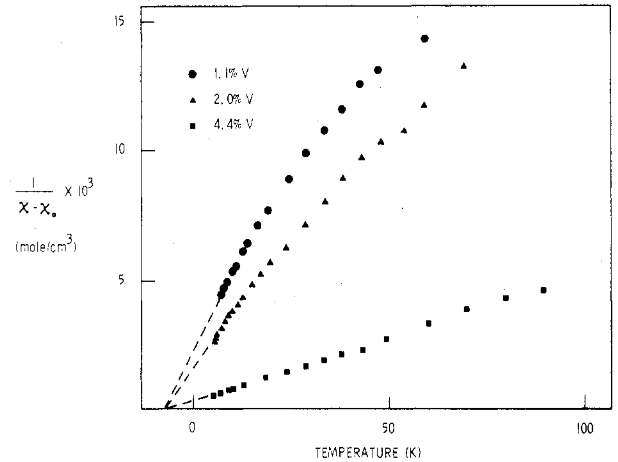

Figure 6. Inverse corrected susceptibility vs. temperature of vanadium-doped niobium disulfides.

The observed magnetic susceptibilities of niobium disulfide appear to be consistent with the qualitative band structure models which have been proposed for transition-metal dichalcogenides.[2,20–22] All the models agree in predicting that stoichiometric NbS_2 should be a Pauli paramagnetic metal. Four of the valence electrons of the niobium go to complete the valence band, and the fifth goes to half-fill the d_{z^2} band. The Fermi surface of 2H-NbS_2 is at or near the center of the narrow d_{z^2} band, so the susceptibility is that of a high-density-of-states, narrow-band metal; the observed high value of χ and its slight temperature dependence may be the result of strong electron–electron correlations, as appears to be the case for $NbSe_2$.[23] In 3R-$Nb_{1+x}S_2$ the interlayer niobium atoms are not magnetic but must donate substantial numbers of electrons to the d_{z^2} band, thus raising the Fermi level. The magnetic susceptibility would then fall with increasing deviation from stoichiometry as the density of states at the Fermi level decreases.

With the phase analytical, superconductivity, and magnetic susceptibility information obtained in this study, the question of whether NbS_2 exhibits a charge-density wave can be addressed. First, we note that there are no kink anomalies observed in the magnetic susceptibilities of either 2H-NbS_2 or 3R-$Nb_{1+x}S_2$ (Figure 4), as are seen in TaS_2 and $TaSe_2$.[24] However, 2H-$NbSe_2$, which has a CDW transition at 35 K, has no anomaly in its susceptibility, either. Hence, magnetic susceptibility offers no evidence for or against a CDW state in 2H-NbS_2 or 3R-$Nb_{1+x}S_2$.

The phase-analytical results show that the 2H polytype is a line phase. Thus, if a CDW is present in this polytype, it is not suppressed by nonstoichiometry. Furthermore, Moliniê, Jêrome, and Grant[25] found no pressure dependence of the

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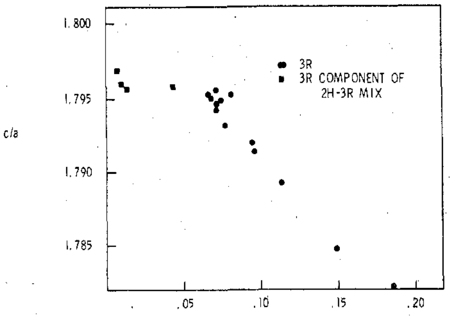

Figure 7. Single-layer c/a ratio vs. x for 3R-$Nb_{1+x}S_2$.

superconducting transition temperature of 2H-NbS_2. Since the effect of pressure on a system exhibiting a CDW is to suppress the CDW and raise the superconducting transition temperature, there must be no such CDW state in 2H-NbS_2.

Thompson[26] has found a correlation between the temperature at which CDW distortion appears and the ionicity of the metal–chalcogen bond as reflected in the single-layer lattice parameter ratio c/a. The distortions may be divided into two groups, on the basis of the temperature dependence of the transport properties. Materials with discontinuities at the distortion temperature are those with octahedral coordination. Their transition temperatures are higher and their c/a ratios are smaller than those for materials with trigonal-prismatic coordination, where transport properties are continuous at the distortion temperature. Only 1T-VSe_2 is an exception to the rule.

If distortion temperatures are plotted as a function of c/a ratio, the zero-temperature intercept of the straight line obtained for materials in the discontinuous group (octahedral) is 1.608; for the continuous group (trigonal prismatic), it is 1.793. As both polytypes of NbS_2 have trigonal-prismatic coordination, they should fall in the continuous group. Therefore a c/a ratio exceeding 1.793 would be required to observe a distortion. In this study, the c/a ratio of stoichiometric 2H-NbS_2 was determined to be 1.798, a value almost identical with the critical ratio for the appearance of a charge-density wave. Hence, no CDW is expected to be observed.

The 3R polytype is a more complicated case as it is nonstoichiometric and c/a changes with stoichiometry. As shown in Figure 7, c/a rises as stoichiometry is approached, but just at the c/a value where the CDW state would be expected to appear, the phase boundary of the 3R-$Nb_{1+x}S_2$ phase is encountered! It seems that appearance of the correct condition for the charge-density wave makes the 3R polytype energetically unfavorable with respect to the 2H polytype. However, it is not clear how an incipient CDW distortion at very low temperature can influence stabilization of a polytype at 750 °C.

One way to test whether an incipient CDW drives the phase transition would be to suppress the CDW chemically, thereby suppressing the phase transition. In this study, we attempted to do this by doping NbS_2 with vanadium. Vanadium has the same number of valence electrons as niobium, so it should not perturb the Fermi surface a great deal. However, its smaller size for a given oxidation state would produce a random potential in the metal atom sublattice, which might suppress the charge-density wave. Unfortunately, all the products turned out to have the 2H structure; i.e., doping with vanadium did not suppress the 3R-to-2H phase change. This does not necessarily rule out a connection between incipient CDW and the 3R-to-2H phase transition. The fact that excess vanadium is magnetic and apparently interlayer suggests that the Fermi surface may not be the same in the doped and undoped systems. Vanadium prefers octahedral rather than trigonal-prismatic coordination; hence, the solubility of vanadium in the layer is probably small. This is consistent with the trend of measured superconducting transition temperatures. The first 1.1% V dropped the transition temperature from 6.3 to 5.3 K; additional vanadium did not produce much effect. This would be the result if the first small amount of vanadium were incorporated in the layer, but additional vanadium went between the layers, where it would have much less effect on the transition temperature.

In the 2H polytype of NbS_2 (Figure 1), the niobium atoms in adjacent layers stack directly one above the other along the c axis. The vacant interlayer site between these niobium atoms is octahedral and presumably is where the interlayer vanadium resides. Thus, we would have the stacking sequence Nb(in one layer)–V(in the gap)–Nb(in adjacent layer) in a direct line. It may be that niobium, being larger than vanadium, cannot occupy a similar gap position, so that when we try to add excess niobium to 2H-NbS_2, the transition 2H to 3R occurs instead, thereby avoiding the sequence Nb(layer)–Nb(gap)–Nb(layer). One way for the 2H-to-3R transition to occur would be for one layer to slide over another and pivot by 60°. However, it is believed that such pivoting is not very likely, as any defect in layer-to-layer registry would pin the layers to each other and interfere with rotation around the c axis. Rather it is believed that the 2H-to-3R transition occurs first by a translational movement of one layer relative to another through the distance $a/3^{1/2}$ in the direction $[12\bar{3}0]$ followed by a second translational movement of the niobium sheet alone through the distance $a/3^{1/2}$ in the direction $[\bar{1}010]$. This converts 2H to 3R, avoids direct stacking of triple sequences Nb–Nb–Nb, and may be the reason going off stoichiometry converts 2H-NbS_2 to 3R-$Nb_{1+x}S_2$.

Whereas excess niobium appears to act in a diamagnetic way, interlayer vanadium clearly shows paramagnetic Curie behavior. There are probably second-order effects arising from difference in polytype (viz., the excess niobium is in 3R, whereas the excess vanadium is in 2H), but the likely main effect is that smaller size and greater ionization potential of vanadium result in greater localization of the d electron.

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(26) A. H. Thompson, *Phys. Rev. Lett.*, **34**, 520 (1975).