

Effect of crystal damage on superconductivity in the transition-metal layer compounds

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The superconducting properties of the transition-metal dichalcogenides TaS_2 , TaSe_2 , NbS_2 , and NbSe_2 have been studied as a function of structural disorder induced by heavy-ion bombardment and by deintercalation at temperatures between 300 and 800 K. Changes in T_c similar to those seen on intercalation by metal ions and organic molecules were observed but there was no increase in the anisotropy of the critical magnetic fields. The changes in T_c are attributed to changes in the electronic structure at the respective Fermi surfaces beyond previously considered changes in the density of states at the Fermi surface on intercalation.

I. INTRODUCTION

The layered-structure transition-metal dichalcogenides have interesting properties as superconductors. The critical temperature (T_c) of these compounds can be readily adjusted and intercalation of metal ions or organic molecules produces either a substantial reduction in the T_c (NbSe_2) or an enhancement in the T_c (TaS_2)^{1,2} and large changes in the magnetic critical fields H_c .³ We report here that the introduction of lattice disorder can produce similar changes in the T_c and H_c of these materials. We have studied the dependence of the superconducting transition temperatures of the metallic transition-metal dichalcogenides TaS_2 , TaSe_2 , NbS_2 , and NbSe_2 on heavy-ion bombardment and structural disorder induced by deintercalation. Previous work on the effects of radiation damage by chemically inert species on T_c in both high- and low-temperature superconductors has reported the observation of the depression of T_c .^{4,5} Our results represent the first observation of an enhancement of T_c due to chemically inert heavy-ion bombardment.

The observation that the intercalation of metal ions and organic molecules can produce apparent changes in the occupation of the d bands has led to a simple interpretation of the changes in T_c of NbSe_2 upon intercalation.⁶ In this model the principal effect of intercalation is to introduce extra electrons into the "rigid" d band, and other effects on the electronic structure are ignored.⁷ In NbSe_2 , this produces a reduction in the density of states at the Fermi level as one goes from a band that is exactly half-filled to one that is more than half-filled. Given the applicability of the simple BCS theory,⁸ a decrease in T_c is observed. This interpretation is unable to explain the observed increase in T_c when TaS_2 is intercalated. It also does not explain the observation of Revelli *et al.*⁹ that the unintercalated mixed compounds $\text{Ta}_x\text{Se}_{2-x}$ and $\text{Nb}_x\text{S}_x\text{Se}_{2-x}$ showed critical temperatures similar to those of intercalated TaS_2 and

NbSe_2 .

Our results support the contention that the simple band-filling model cannot account for the substantial changes observed in T_c in these compounds upon intercalation. We believe that the changes observed by us in the disordered phases of TaS_2 and by others in the intercalated phases of TaS_2 are due to the quenching of structural phase transitions upon intercalation or disordering and to the associated quenching of changes in the density of states at the Fermi surface and in addition, possibly, the magnitude of the electron-phonon interaction.

II. EXPERIMENTAL DETAILS

Measurements were made on both single crystals and powdered samples. The single crystals were grown from prereacted powders by an iodine-vapor transport technique at temperatures between 1200 and 1300 K. The samples studied were annealed at about 1200 K to produce the 2S polytype and were characterized by their x-ray diffraction patterns using copper $K\alpha$ radiation.

Structural disorder was introduced into these materials by two means. Single-crystal samples were subjected to heavy-ion bombardment at various fluences. Samples were exposed to 10^{17} protons/cm² at 180 keV, from 10^{13} to 10^{17} argon ions/cm² at 180 keV, and a variety of metallic ions in the 10^{17} /cm² range, also at 180 keV. All the irradiations were done at room temperature. No detailed structural studies of the radiation-induced damage were possible because of the limited penetration depths (~ 2000 Å) of the heavy ions used in this study. Since the penetration depth of the heavy ions was considerably less than the penetration depth of the normally incident x rays used in our structural studies, the x rays predominantly sampled the undamaged bulk rather than the damaged region near the surface.

The argon ions used in the bombardment studies are inert and cannot contribute any electrons to the

host crystal. As a result, the principal effect of the argon ions is a geometric one, that of creating various types of isolated and collective defects rather than a chemical one. Since the crystal bonding in these compounds is predominantly ionic and/or covalent and only weakly metallic, it is expected that the chief effect of the heavy-ion bombardment will be to create localized crystal defects. Because of the reversible character of the damage on annealing at relatively low temperatures and the difference in the behavior of the Ta and Nb compounds, we believe that the effects of chalcogenide ion loss in our systems are negligible.

Single crystals and powdered samples were also damaged by a process of intercalation by molecules such as ammonia or dioxane followed by deintercalation at relatively low temperatures ($300\text{ K} < T < 800\text{ K}$). The deintercalation process consisted of holding the sample in a vacuum of better than 10^{-6} Torr at a temperature between 300 and 800 K for a fixed length of time (usually 16 h). It was found that certain high-vapor-pressure intercalates could be pumped out of the crystals at temperatures below that required to anneal the damage associated with the deintercalation process. The x-ray diffraction patterns of crystals so treated showed dramatic changes as a function of the temperature at which deintercalation was carried out, and these will be discussed in Sec. III.

The superconducting transition temperatures were obtained through measurements of the resistivity of the single-crystal samples and magnetization of both single crystals and powders. The resistivity was measured by a conventional four-wire ac technique at 11 Hz. The samples measured were cut into thin bars 4 or 5 mm long

and about 1 mm wide. The sample thicknesses ranged between 0.05 and 0.25 mm and the current levels used ranged between $10\ \mu\text{A}$ and 10 mA. No significant dependence of T_c on the current used was observed. The critical magnetic fields required for the destruction of superconductivity were obtained through the magnetoresistance of the samples. The magnetic fields used were generated by a 50-kG superconducting solenoid. The low-frequency magnetic susceptibility was measured by a mutual inductance technique at 11 Hz. The temperature was measured by a carbon resistor and by monitoring the vapor pressure of the liquid-helium bath. The lowest temperature measured in the experiment was 1.2 K and all temperatures were measured to well within 0.1 K.

III. RESULTS

A. Structure

As mentioned above, no structural studies were made on the argon-bombarded samples. However, gross changes in the structure of ammonia- and dioxane-deintercalated samples were observed. Chemical and thermogravimetric analysis performed on the TaS_2 samples deintercalated at different temperatures showed that substantial amounts of intercalated ammonia were lost during deintercalation. With the exception of a small residue of ammonia that would not deintercalate at any temperature, it was observed that most of the intercalated ammonia was expelled from the crystal at temperatures as low as 600 K. The dependence of the amount of ammonia in the sample on the deintercalation temperature is shown in Fig. 1. A residual of about 15% of the originally intercalated NH_3 does not deintercalate for $T < 1000\text{ K}$. We shall see that major changes in the crystal structure and the superconducting properties of TaS_2 occur for temperatures below 600 K and that changes in the amount of intercalate are relatively unimportant for $T < 600\text{ K}$.

The x-ray diffraction patterns for the (002) reflection in pure, intercalated, and deintercalated TaS_2 shown in Fig. 2 indicate that substantial changes in the crystal structure of the TaS_2 occur as the intercalate is removed. Figure 2 (a) shows the diffraction pattern obtained from pure TaS_2 that has been fully intercalated with ammonia. The succeeding figures correspond to the x-ray patterns of samples that have been held for 16 h in a vacuum at the temperatures indicated in the figure. The extremely sharp (002) reflection both broadens and shifts slightly if the sample is held at about room temperature. Figure 2 (b) also shows the appearance of a considerably broader band which occurs at higher angles and therefore

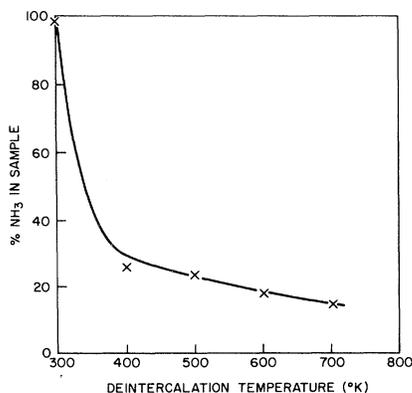


FIG. 1. Dependence of the concentration of intercalated ammonia in $\text{NH}_3 - \text{TaS}_2$ (2S) on temperature for isochronal anneals at 10^{-6} Torr pressure. 100% represents fully intercalated material.

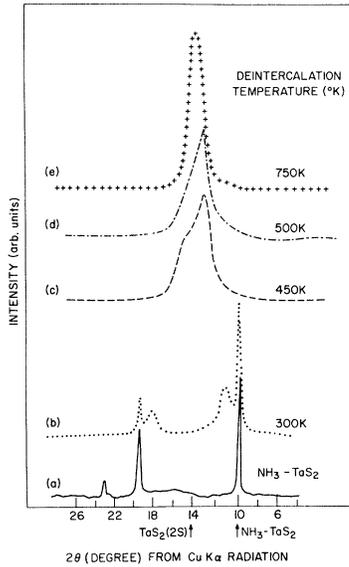


FIG. 2. X-ray diffraction patterns for $\text{NH}_3\text{-TaS}_2$ (2S) subjected to (a) no deintercalation, (b) deintercalation at room temperature, (c) deintercalation at 450 K, (d) intercalation at 500 K, and (e) deintercalation at 750 K. Positions of (002) peaks for the pure unintercalated and the fully intercalated material are indicated at bottom.

corresponds to reflections from smaller lattice constants. Dramatic changes in the diffraction pattern are observed if the sample is held for 16 h at 450 K. In Fig. 2 (c), we find that the (002) reflection observed in the fully intercalated material is absent, and in its place we observe a broad line extending to considerably larger angles (up to 16°) and therefore corresponding to a range of smaller lattice constants. The peak of the line occurs at a value well below that observed in the pure unintercalated material. It is also observed that the higher-order reflections are missing. As the temperature at which the sample was deintercalated is increased, we find that the broad line shown in Fig. 2 (c) shifts to higher angles and begins to narrow [Figs. 2 (d) and 2 (e)]. At temperatures of about 800 K, the observed pattern closely resembles that of pure, unintercalated TaS_2 in both position and width, and the higher-order lines reappear. The width of the (002) reflections, the intermediate position of the maxima of the (002) reflections, the quenching of the higher-order reflections, and the asymmetric shape of these lines all provide strong evidence that the deintercalated material is strongly disordered with both significant disordering of the individual layers and a loss of registry between the layers. Guinier camera x-ray patterns for pure ammonia-intercalated TaS_2 and deintercalated TaS_2 show that *all* of the diffraction lines in the

deintercalated material are significantly broadened in comparison with the homogeneous material. We conclude that the samples deintercalated at temperatures between 400 and 700 K show substantial lattice disorder. The reappearance of x-ray diffraction patterns similar to those of the pure unintercalated material for temperatures of deintercalation in excess of 800 K is evidence that this damage recovers at temperatures above 800 K. No evidence in x-ray diffraction was observed for the formation of a metallic overlayer due to selective sputtering of the chalcogenide ions.

Our x-ray diffraction system was capable of observing the formation of a 2S polytype layer of TaS_2 on 1S TaS_2 following 180-keV heavy-ion bombardment and should have been capable of observing the formation of a Ta overlayer. Efforts to intercalate NbSe_2 with ammonia generally produced mixed-phase material that tended to decompose into pure unintercalated NbSe_2 at room temperature. The decomposed product was identical to pure NbSe_2 and no evidence of substantial lattice disorder was observed.

B. Electrical properties

The superconducting parameters of TaS_2 and TaSe_2 were strongly affected by the introduction of crystal disorder. The results of measurements of T_c and the ratio of the magnetic fields H_c required to destroy superconductivity for H_c parallel to the c axis and H_c perpendicular to the c axis are given in Table I. We shall first discuss the changes in the critical temperature and the resistivity of the samples upon damage and then consider the changes in the anisotropy of H_c .

A single-crystal sample of TaS_2 ($T_c = 0.8$ K)¹ showed a $T_c = 4.2$ K after bombardment by 10^{17} argon ions/cm² at 180 keV. The resistive transition was about 0.3 K wide (Fig. 3). In Fig. 4 we show that as the fluence was decreased, T_c for the resistive transition decreased and the width of the transition increased. A sample of TaSe_2 ($T_c = 0.15$ K) subjected to bombardment by 10^{17} argon ions/cm² at 180 keV showed a superconducting transition beginning at 2.5 K. In both cases, T_c before bombardment was measured to be below 1.2 K.

The enhancement of T_c in these crystals by ion bombardment can be reversed by annealing in a vacuum of better than 10^{-6} Torr. A TaS_2 sample bombarded by 10^{17} Ar ions/cm² and then annealed at 500 K showed a decrease of T_c from about 4.2 K to about 2.0 K. Subsequent anneals at higher temperatures reduced the transition temperature to below 1.2 K as can be seen in Fig. 4.

As mentioned above both powder and single-

TABLE I. Electrical and superconducting parameters of pure, intercalated, deintercalated, and radiation-damaged TaS₂ (Refs. 1, 3, and 9).

| Material | T_c (K) | $\frac{H_{cII}}{H_{cI}}$ | $\frac{\rho_x(10\text{ K})}{\rho_{\text{TaS}_2}(10\text{ K})}$ | $\rho(T)$ |
|--|--|--------------------------|--|----------------------------------|
| TaS ₂ (2S) | 0.7 | N.A. | 1 | Shows elbow at 70 K |
| TaSe ₂ (2S) | 0.15 | N.A. | ... | Shows elbow at 110 K |
| NbS ₂ (2S) | 6.3 | N.A. | ... | ... |
| NbSe ₂ (2S) | 7.0 | 3.5 | ... | Shows elbow at 30 K |
| TaS _x Se _{2-x} (0.2 < x < 1.8) (2S) | 2.0 < T < 3.8 | 6.5 | 3 | Does not show elbow in $\rho(T)$ |
| NbS _x Se _{2-x} (0.2 < x < 1.8) (2S) | 3.0 < T < 6.0 | N.A. | ... | ... |
| TaS ₂ (2S) deintercalated at 200 K | 3.8 | 4 | 2.0 | Does not show elbow in $\rho(T)$ |
| TaS ₂ bombarded 10 ¹⁷ Ar/cm ² | 4.2 | 3.5 | N.A. | ... |
| TaS ₂ (2S) inter- calated NH ₃ | 3.8 | 10 | 1.5 | Does not show elbow in $\rho(T)$ |
| TaSe ₂ (2S) bom- barded 10 ¹⁷ Ar/cm ² | 2.5 | N.A. | ... | ... |
| TaSe ₂ (2S) inter- calated pyridine | 2.5 | N.A. | ... | Does not show elbow in $\rho(T)$ |
| NbSe ₂ (2S) bom- barded 10 ¹⁷ Ar/cm ² | T_c showed no change indicating that T_c did not increase under heavy-ion bombardment. | | | |

crystal samples were subjected to deintercalation. The ammonia- and dioxane-intercalated TaS₂ powders showed T_c 's similar to those previously reported.² The powdered samples and single crys-

tals deintercalated at temperatures below 600 K showed T_c 's well above 3 K. The transitions for both the intercalated samples and the deintercalated samples were extremely broad, often in excess of 1 K. The critical temperatures for the super-

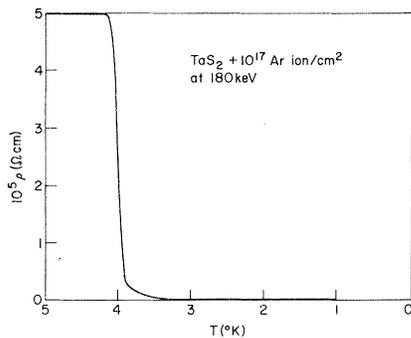


FIG. 3. Low-temperature resistivity of TaS₂ after bombardment by 10¹⁷ argon ions at 180 keV.

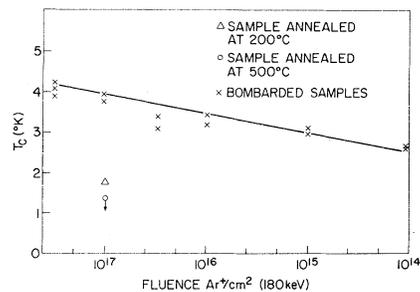


FIG. 4. Dependence of the superconducting transition temperature T_c of TaS₂ (2S) on fluence of 180-keV argon ions.

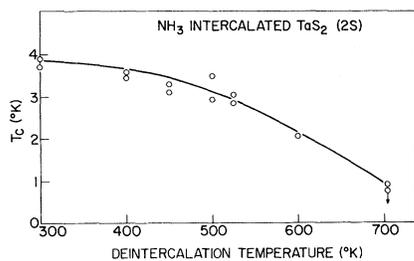


FIG. 5. Variation of T_c for deintercalated $\text{NH}_3\text{-TaS}_2$ as function of temperature of deintercalation.

conducting transition in the deintercalated samples show only a slight decrease until the deintercalation temperature goes above 500 K (Fig. 5). This temperature is above that at which most of the ammonia is pumped out of the sample (Figs. 1 and 6) and in the range of temperatures where the damage as seen in x-ray studies is beginning to anneal away.

As can be seen in Fig. 7 the temperature dependence of the resistivity of the deintercalated single crystals of TaS_2 also showed substantial changes from the case of the pure unintercalated samples. It strongly resembles that of the single-phase intercalated material in that the break or elbow in the resistivity at a temperature of about 70 K is no longer present. This break has been associated by Thompson *et al.*⁷ with a change in the sign of the Hall coefficient of TaS_2 at this temperature and is thought to reflect a small structural phase transition. The resistivity at low temperatures substantially differs from that of the pure material and the fully intercalated material in that it is considerably greater than either (Table I). The enhanced value of the low-temperature residual resistance is presumably due to enhanced impurity scattering associated with the high degree of crystal disorder present.

The deintercalation of these samples produced T_c 's comparable to the T_c 's of the intercalated samples for deintercalation temperatures below

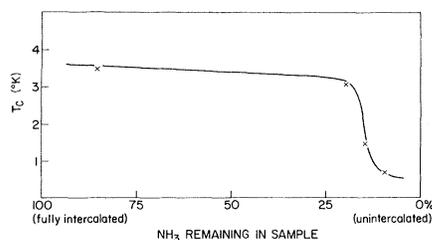


FIG. 6. Variation of T_c for deintercalated TaS_2 as function of ammonia concentration in sample. 100% NH_3 represents fully intercalated material.

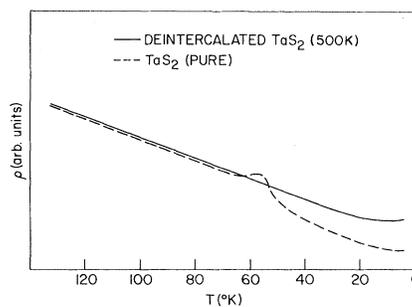


FIG. 7. Temperature dependence of resistivity of pure TaS_2 and deintercalated $\text{NH}_3\text{-TaS}_2$ (2S) showing the absence of an "elbow" in latter at 70 K.

600 K. The deintercalation process produced anisotropy ratios for the critical magnetic field H_c considerably lower than was the case in the fully intercalated materials. Typically, in pure NbSe_2 and in the mixed system $\text{TaS}_x\text{Se}_{2-x}$, the value of $H_{c||}/H_{c\perp}$ is under 6, where $H_{c||}$ is the field required to destroy superconductivity for H parallel to the c axis and $H_{c\perp}$ is that required to destroy superconductivity for H perpendicular to the c axis.³ In pyridine- and ammonia-intercalated TaS_2 , the anisotropy ratio is considerably greater, with values in excess of 30 being common.³ The anisotropy ratio for the critical magnetic field of the deintercalated samples and for the argon-ion-bombarded samples was, in all cases, in the range 2.8–4.0 (Table I).

The principal physical effect of intercalation of either metallic ions or organic molecules is the enhancement of the c -axis length. In the case of intercalation by pyridine in TaS_2 , the c axis for the unit cell changes from about 12 to 18 Å.⁷ One consequence of this change is the enhancement of the anisotropy ratio of the critical magnetic field for the destruction of superconductivity.³ We interpret the fact that the ratio of the critical fields parallel and perpendicular to the c axis in deintercalated samples is less than that of the intercalated material as indicating that the elevated critical temperatures observed by us are not due to the presence of filaments of intercalated material sitting in a host of nonintercalated material. The superconductivity associated with filaments of intercalated material should show H_c 's above those of the pure compounds.

As mentioned earlier, deintercalation of NbSe_2 samples did not produce the dramatic crystallographic changes observed in the case of TaS_2 and TaSe_2 . The deintercalated NbSe_2 samples showed the same structure as that of pure NbSe_2 , and as might be expected they showed no enhancement of T_c . Samples of NbSe_2 bombarded by argon ions at

180 keV also showed no enhancement of T_c . In both of these cases, the presence of well-ordered regions of NbSe_2 would have made it impossible to observe any significant depression of T_c since the resistivity of the disordered region would be shorted out by the pure single-crystal material. As mentioned earlier, it is known from the work of Revelli⁹ that the critical temperature of the mixed system $\text{NbS}_{2-x}\text{Se}_x$ is depressed with respect to the critical temperature of the pure phases.

IV. DISCUSSION

Recently, considerable work has been done on (i) the effects of heavy-ion bombardment on elemental superconductors, (ii) the superconducting properties of d -band metals, and (iii) the electronic structure of the group VB transitional-metal dichalcogenides. We shall briefly mention some of the above work before attempting to consider some of the implications of our experimental results.

A. Radiation damage and superconductivity

Recently, Meyer *et al.*⁴ reported on the effects of heavy-ion bombardment on the T_c 's of the simple transition metals and a number of the simple cubic compounds of Nb. The results were explained in terms of the changes in the electronic structure of the implanted material through the BCS theory. The decrease in T_c upon bombardment by inert ions was attributed to changes in the density of states of the damaged metal since the radiation damage was thought to smooth out any sharp anomalies in the density of states. In those cases where the Fermi surface corresponded to a maximum in the density of states, this would result in a reduction in the density of states at the Fermi surface and a reduction in T_c .

Since the changes in T_c of TaS_2 and TaSe_2 upon bombardment by argon ions are positive, i. e., T_c increases, the model used by Meyer *et al.* is probably not appropriate for these. This is especially true since Ar^+ bombardment of the closely related niobium dichalcogenides does not produce this effect, and in both cases the density of states at the Fermi surface is thought to be very high and the Fermi surface occurs at or near a maximum in $N(E)$. As a result it seems reasonable to assume that the changes in T_c have their origin in more subtle changes in the electronic structure or in the phonon spectrum.¹ T_c enhancements have been observed in amorphous films laid down at 4.2 K and these enhancements have been attributed to changes in the phonon density of states between the pure and the amorphous phases.¹⁰

B. Superconductivity in d -band metals

Considerable work has recently gone into the effort to understand systematic trends in the su-

perconducting properties of the transition metals and their compounds.¹¹⁻¹⁴ Chui¹³ recently showed that in those situations where the wave function ψ at the Fermi surface is strongly hybridized, i. e.,

$$\psi = a\psi_d + b\psi_{sp},$$

where ψ is the wave function at the Fermi level, ψ_d is the d -band wavefunction, ψ_{sp} is the s - p wavefunction, and a and b are mixing coefficients, the dominant contribution to the electron-phonon interaction comes from those matrix elements connecting the hybridized plane waves to the localized d wave functions. The contribution due to the overlap of adjacent d orbitals to the electron-phonon interaction should be orders of magnitude smaller in the transition metals, according to Chui.

Since the distance between neighboring metal ions in the transition-metal dichalcogenides is 15% larger than in the simple metals, we are forced to conclude that the contributions of the tight-binding terms to the electron-phonon matrix elements in the layer compounds are *also* small and that the hybridization terms are dominant.

C. Electronic structure of the transition-metal dichalcogenides and superconductivity

The band structures¹⁴⁻¹⁸ of the transition-metal dichalcogenides are considerably different from those of the simple transition metals. This is due to the strong interaction between the metal s and chalcogenide p electrons which results in the creation of a bonding-antibonding gap. Furthermore, ultraviolet and x-ray photoemission data¹⁵ indicate that the position of the d band within the bonding-antibonding gap shows significant variations from compound to compound. In TaS_2 it has been observed that the d band sits well above the top of the chalcogenide p band, while in NbSe_2 the lowest-lying d band occurs as a shoulder on the high-energy side of the p band. In all cases, the d bands are narrow and the density of states at the Fermi surface is extremely high.

Recently, it was shown that the high density of states at the Fermi surface coupled with the high anisotropy of these systems produced Fermi-surface anomalies that were responsible for the observed anomalies in ρ and R_H at low temperatures.¹⁹ The introduction of superlattices in these compounds at low temperatures produces large changes in the density of states at the Fermi surface and also changes in the phonon spectrum. In such a transition the density of states at the Fermi surface will always be reduced as one goes from the high-temperature phase to the more stable low-temperature phase. Therefore, stabilization of the high-temperature phase would tend to enhance T_c . If this is the case, then the behavior

of the Nb compounds in the mixed crystal phase is strange since there T_c decreases upon stabilization. This could be explained by arguing that the change in the density of states at the Fermi surface of the Nb compounds is opposite to that in the Ta compounds. However, this argument is inconsistent with evidence¹⁶ which shows that the density of states in the Nb compounds is higher than in the Ta compounds and with the theoretical fact that if the transition in question is driven by the existence of a very high density of states at the Fermi surface, it should always produce a substantial decrease in the density of states at the Fermi surface. Similarly, any changes in the phonon spectra associated with the low-temperature phase transition cannot, by itself, explain the difference in the behavior of T_c in the Ta and Nb compounds since the changes in T_c for the two compounds should be in the same direction. In addition, since the phase transition appears to be of an exceedingly fine character¹⁹ it is unlikely that it can have a major effect on the phonon density of states.

It is of course possible that the phase transition observed by Wilson *et al.* produces both changes in $N(E_f)$ and the phonon spectrum where the former would tend to depress T_c and the latter enhance T_c . Therefore, when the transition is quenched T_c would decrease if the change in the density of states were large and negative and increase if the mean phonon frequency moved to lower energies.

The superconducting transition temperature is known to depend on three quantities, the density of states at the Fermi surface, the phonon spectrum, and the electron-phonon interaction.¹¹ Most past work has tended to concentrate on the changes in T_c associated with changes in the density of states or the phonon spectrum. We would like to point out that there are a number of reasons to expect that in the layer compounds, the process of intercalation or the introduction of lattice disorder can produce substantial changes also in the electron-phonon interaction. As a result, any attempt to understand the changes that occur in T_c upon intercalation or disordering must consider all three parameters.

As mentioned earlier, the d bands sit within the s - p bonding-antibonding gap in the VB transition-metal dichalcogenides. Huisman *et al.*²⁰ pointed out that the overlap of the p - d bands reflected the covalent mixing of the d wave functions with the chalcogenide p ligands. They showed that the position of the d band within the bonding-antibonding gap of these compounds is a very sensitive function of the detailed crystal structure, the trigonal prismatic phase in fact only being stabilized by the mixing of the d wave functions and

the chalcogenide ligands. In our experiments the introduction of substantial crystalline disorder both quenches the crystallographic phase transition and introduces a slight broadening of the bands. Both of these effects can produce a change in the p - d overlap at low temperatures. This change in the relative positions of the p and the d bands in the low-temperature phases of the pure and the intercalated and disordered compounds would produce differences in the hybridization of the d electrons at the Fermi surface and could produce large changes in the electron-phonon coupling at the Fermi surface. This change would of course have to be considered in an effort to explain the changes in T_c that are observed in these systems.

Further evidence for our point of view can be obtained on the basis of recent unpublished work by Kasowski.¹⁷ In this work, Kasowski finds that the process of intercalation produces large changes in the band structure, especially in the details of the d bands. Furthermore, he finds that the band structure is sensitive to small changes in crystal structure and that a simple rigid-band-type approach is inadequate to represent the changes that occur upon intercalation. Given these large changes in the band structure, it becomes no longer correct to assume that the electron-phonon interaction remains the same independent of whether the crystallographic transition has occurred.

V. CONCLUSION

We have considered the effects of small changes in the electronic structure on the critical temperature T_c of the superconductors TaS₂, TaSe₂, NbS₂, and NbSe₂. We find that many of the effects on T_c previously associated with intercalation can be duplicated with the introduction of crystallographic disorder by either low-temperature deintercalation or by heavy-ion bombardment. Our observation that the T_c 's of TaS₂ and TaSe₂ are enhanced by radiation damage may be contrasted with the measurements of Meyer *et al.*⁴ and Sweedler *et al.*⁵ in which T_c is always depressed by radiation damage. In the case of the 2S polytypes of TaS₂ and TaSe₂ we find that the quenching of a structural phase transition can produce an enhancement of T_c . We associate the changes in the critical temperature upon intercalation and the introduction of crystal disorder with the quenching of the phase transitions⁵ in these compounds that normally occur in the temperature region between 20 and 80 K.

The changes in T_c observed by us can be due to changes in the character of the electron-phonon interaction at the Fermi surface upon intercalation or disordering in addition to the previously

considered changes in $N(E_F)$ and $\langle \omega^2 \rangle$. We find that the changes in T_c we observed cannot qualitatively be explained either by a band-filling model based on the rigid-band model or a mode softening model. Recent band-structure calculations on these compounds make it evident that the changes in the band structure upon intercalation or disordering are sufficiently large that changes

in all three parameters must be considered in any attempt to explain the changes in T_c .

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