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Charge Density Wave Transitions Induced in Nb_3Se_4 and Nb_3S_4 by Indium Intercalation

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The family of crystals Nb_3X_4 (X = Te, Se, S) are isostructural, quasi one-dimensional tunnel structures. The telluride exhibits a charge density wave below room temperature, but no such transition occurs in the selenide or sulfide. A variety of foreign atoms can be intercalated into the tunnels of these structures and it is known that thallium intercalation in Nb_3Te_4 causes dramatic changes in the charge density wave characteristics, due to changes in the Fermi surface and density of states resulting from the electrons being transferred to the host crystal from the intercalated atoms. In this paper it is shown that indium intercalation in Nb_3Se_4 and Nb_3S_4 gives rise to superlattice reflections in electron diffraction patterns, which are interpreted as being due to charge density waves. The unusual variations of the charge density wave vectors with intercalate concentration are discussed and a model to account for them is proposed. © 1999 Academic Press

Key Words: **charge density waves; intercalation; triniobium tetrachalcogenides; electron diffraction.**

INTRODUCTION

Charge density wave (CDW) modulated crystals are of interest because of their unusual electronic properties and possible technological applications of these phenomena (1–4). However, the variation of CDW characteristics with changes in the electronic structure and the nature of the interactions of the modulation waves with defects and impurities are not well understood. The reason for this, in large part, is because attempts to experimentally investigate these problems have been thwarted by the fact that substitutional impurity atoms (dopants) generally lower the CDW transition temperatures and rapidly quench the CDW due to impurity interactions and disorder. These effects also inhibit the possibility of using the electronic changes associated with doping to induce CDW formation in materials which do not exhibit this phenomenon in the pure state. We have recently attempted to circumvent this difficulty by studying CDW in quasi-one-dimensional tunnel structures in which large fractions of foreign atoms can be intercalated in the tunnels without introducing atomic disorder along the metal atom chains that support the CDW. Nb_3Te_4 is a member of the family of isostructural crystals Nb_3X_4 (X = Te, Se, S). These crystals are quasi-one-dimensional, hexagonal conductors with space group ($P6_3/m$) (5). Large tunnels, in which a variety of foreign atoms can be intercalated, run parallel to the fiber axes (6, 7). A CDW occurs in pure Nb_3Te_4 at about 95 K and we have shown that indium or thallium intercalation in these crystals does not inhibit the CDW formation but instead produces dramatic increases in both the CDW transition temperatures and characteristics (8, 9). For the case of $Tl_xNb_3Te_4$, the variation in the transition temperatures and wave vectors with x was interpreted in terms of the rapid change in the electron density of states at the Fermi level, $D(E_f)$, as the electrons from the intercalate ions were added to the host crystal conduction band.

There has been previous interest in the Nb_3X_4 (X = Te, Se, S) family of crystals because they exhibit superconductivity at very low temperatures, and several workers have performed calculations of the band structures and Fermi surfaces (10–12). The Fermi surfaces for all three crystals are similar and the Fermi energy is near a minimum

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in the density of states curve in each case. The Fermi-level density of states is 2.28, 3.17, and 2.20 states/(eV/molecule) for Nb_3Te_4, Nb_3Se_4, and Nb_3S_4, respectively. It is not immediately evident why the telluride exhibits a CDW while the selenide and sulfide do not. It has been reported by Oshiyama (10) that the ratio of the conduction bandwidth along the chain to that in the perpendicular direction is about 19 for Nb_3Te_4, 18 for Nb_3Se_4, and 15 for Nb_3S_4, which indicates that the interactions between the Nb atom chains in somewhat less in the telluride than in the selenide and sulfide. This view is reinforced by X-ray diffraction single-crystal structural data, which shows that the Nb–Nb atom spacings within the chains is less than that between the chains by 22.9, 16.8, and 14.5% for the telluride, selenide, and sulfide respectively (13, 14). Thus, the Nb atom chains have the most quasi-one-dimensional character for the telluride and this may account for the fact that it exhibits a CDW in the pure state. Canadell and Whangbo (12) suggested that alkali metal intercalation of the crystallographically similar Ti_3X_4 (X = Se, S) would shift the Fermi level to a higher value of $D(E_f)$ and might result in interesting changes of the physical properties, but no such experiment has so far been carried out. Thus, in view of our previous results on the enhancement of the CDW transition in intercalated Nb_3Te_4, it appeared that increases in interchain screening together with a larger $D(E_f)$ might lead to new CDW in intercalated Nb_3Se_4 and Nb_3S_4. We therefore examined $In_xNb_3Se_4$ and $In_xNb_3S_4$ single crystals as a function of composition and temperature using electron diffraction. For both of these materials we found strong diffraction evidence for CDW, as well as unusual diffraction effects attributed to one-dimensional ordering of the In ions in the tunnels. The experiments are described and the results are discussed in this paper.

EXPERIMENTAL

The crystals were grown from the elements in evacuated quartz tubes using iodine as the transport agent. The materials were placed in the cooler ends of the tubes which were heated to 990°C for Nb_3Se_4 and to 1010°C for Nb_3S_4. Gradients of about two degrees per centimeter were established along the tubes. Fibrous single crystals up to several centimeters in length were obtained after 10 days. Crystals were crushed between glass slides to obtain finer fibres and these were weighed and sealed in evacuated quartz tubes with amounts of In wire appropriate for the desired compositions. The tubes containing $In_xNb_3Se_4$ were annealed at 600°C for 12 days, then 400°C for a further 12 days; those containing $In_xNb_3S_4$ were annealed at 500°C for 20 days. No compositional analyses were carried out but results varied smoothly and reproducibly with nominal indium contents, x, in $In_xNb_3Se_4$ and $In_xNb_3S_4$ up to $x = 0.5$. For $x > 0.5$ residual indium could be detected and there were no significant changes in the diffraction results for nominal values of x in the range from 0.5 to 1.0. Several crystals examined from each run gave identical results, indicating that the In was taken up uniformly by the samples. We conclude that the actual compositions are close to the nominal values for x up to 0.5 and that this corresponds to the maximum amount of In that can be taken up by the crystals under the annealing conditions used.

Specimens for electron diffraction were prepared by selecting a few of the intercalated crystals, crushing them between glass slides, and picking them up on sticky copper grids. Usually, several crystals with suitably thin areas could be found. These crystals were examined in an electron microscope at 100 kV using a double-tilt specimen holder that could be cooled with liquid nitrogen or helium. The lowest temperature attainable was 27 K.

RESULTS

Indium intercalation in both the Nb_3Se_4 and Nb_3S_4 resulted in electron diffraction SL (superlattice) reflections, which we attribute to CDW, and whose positions are described by wave vectors, $\mathbf{q}$, where

$$\mathbf{q} = \pm(\tfrac{1}{3}\mathbf{a}^* + \tfrac{1}{3}\mathbf{b}^*) + z\mathbf{c}^*$$

and $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ are reciprocal lattice vectors. We found that the components along $\mathbf{a}^*$ and $\mathbf{b}^*$ were independent of intercalate content; however, the component along the fiber axis, $\mathbf{q}_c = z$, is determined by the Fermi surface nesting condition and is expected to be a function of composition. In this paper we will consider only $\mathbf{q}_c$, which we will refer to as the CDW wave vector. We note that the SL spot positions associated with the CDW that occurs at low temperature in pure Nb_3Te_4 are described by the above equation with $z = 0.429$ (15). The variations in the CDW wave vectors with composition in the intercalated selenides and sulfides were similar but there were significant differences in the detailed observations so that results for each compound are described separately.

$In_xNb_3Se_4$

The lowest concentration for which SL spots were detected at 90 K was $x = 0.20$ and in these samples the spots were very diffuse and weak. The wave vector was estimated to be $\mathbf{q}_c = 0.41 \pm 0.02$. For $x = 0.25$ the SL spots were still diffuse but somewhat stronger and the wave vector had increased to $\mathbf{q}_c = 0.44 \pm 0.02$. For $x = 0.29$ the spots were still diffuse, stronger, and the wave vector increased to $\mathbf{q}_c = 0.47$, such that the diffuse SL pairs were just-resolved. At $x = 0.33$ there was a dramatic change in the patterns: at 90 K, very sharp SL spots appeared at $\mathbf{q}_{c1} = 0.425 \pm 0.003$ and a set of much fainter, diffuse SL spots occurred at $\mathbf{q}_{c2} = 0.40 \pm 0.01$.

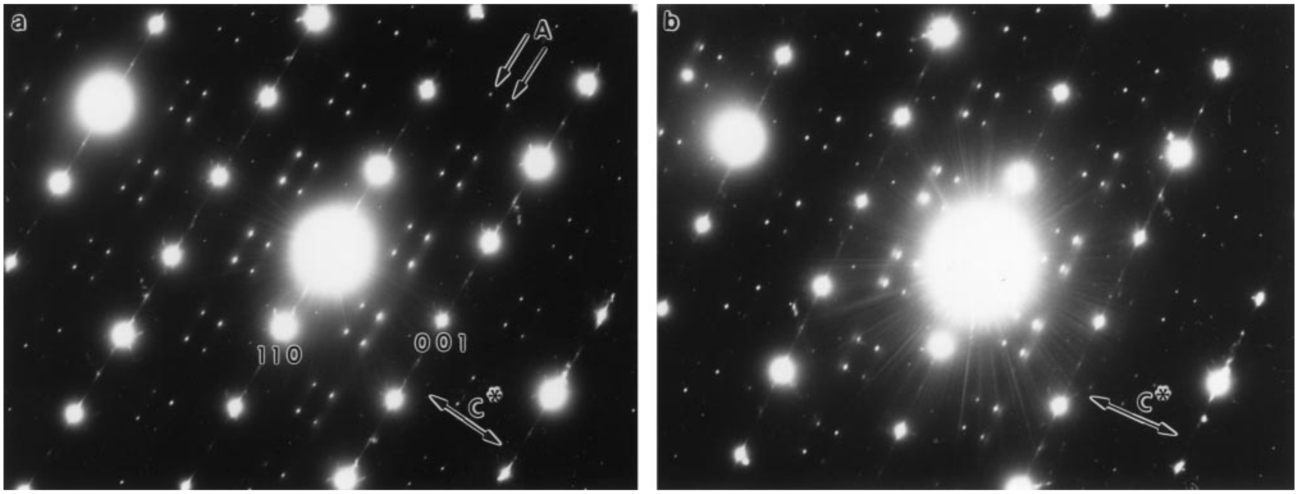

FIG. 1. Electron diffraction pattern of $In_{0.33}Nb_3Se_4$ showing the $(1\bar{1}0)^*$ reciprocal lattice plane (a) at 90 K, rows of sharp superlattice spots occur as indicated by arrows, A. Very faint diffuse superlattice spots can be detected just outside the sharp spots. (b) At 26 K two sets of sharp superlattice spots are clearly resolved.

A diffraction pattern from this sample is shown in Fig. 1a. On cooling to 26 K the diffuse spots became sharper and there was no significant change in the $\mathbf{q}$ vectors (Fig. 1b). When the intercalate concentration increased to $x = 0.40$, faint, very diffuse SL spots could already be detected at room temperature, which were estimated to correspond to a wave vector $\mathbf{q}_c = 0.33$. On cooling to 90 K, the patterns exhibited both sharp SL spots at $\mathbf{q}_{c1} = 0.425$ and diffuse spots at the commensurate position $\mathbf{q}_{c2} = 0.333 \pm 0.003$ (Fig. 2). For $x = 0.50$ very diffuse SL spots were again observed in room temperature patterns. However, at 90 K the sharp SL spots were no longer present and the diffuse spots had moved to $\mathbf{q}_{c2} = 0.311 \pm 0.003$. In addition, at this composition lines appeared lying close to and on each side of the main spot rows perpendicular to $\mathbf{c}^*$. There was a very slight intensity modulation along the lines. These features can be seen in Fig. 3. At 26 K the lines were somewhat sharper but the modulation remained very slight. For compositions in the range $0.5 < x \leq 1.0$ the diffraction patterns were the same as those for $x = 0.50$.

$In_xNb_3S_4$

For the sulfide the effects of indium intercalation were similar to those noted above for the selenide but the initial changes occurred for lower values of x in $In_xNb_3S_4$ as compared to $In_xNb_3Se_4$. Thus, at $x = 0.20$ faint, diffuse SL spots were observed at 90 K with $\mathbf{q}_c = 0.47 \pm 0.01$, which is similar to the result for $In_xNb_3Se_4$ with $x = 0.29$. For $x = 0.25$, the diffuse SL spot pairs were not resolved at 90 K (Fig. 4a), indicating a $\mathbf{q}_c$ value very close to 0.50. On cooling this specimen to 26 K, the spots were much sharper and clearly resolved (Fig. 4b), giving $\mathbf{q}_c = 0.486 \pm 0.002$. For $x = 0.33$, at 90 K, the diffuse spots had shifted to give $\mathbf{q}_c = 0.39 \pm 0.01$. We note that in contrast to the case for the selenides, where two sets of SL spots were observed for certain compositions, only a single set of spots was detected in all the sulfide samples. For $x = 0.40$ faint, very diffuse SL spots were observed in diffraction patterns at room temperature. At 90 K the SL spots were stronger and diffuse giving $\mathbf{q}_c = 0.213 \pm 0.005$. In addition, very faint lines were detected lying close to the main spot rows perpendicular to $\mathbf{c}^*$. For $x > 0.4$ the only change was that the lines became

FIG. 2. Electron diffraction pattern of $In_{0.40}Nb_3Se_4$ showing the $(1\bar{1}0)^*$ reciprocal lattice plane at 90 K. A slightly diffuse set of superlattice spots occurs along rows such as indicated by arrows at A and a second, sharper, set of superlattice spots occurs along rows such as indicated by arrows at B.

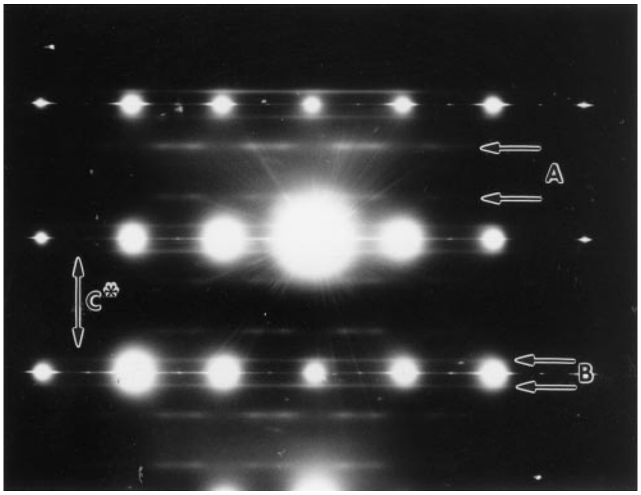

FIG. 3. Electron diffraction pattern of $In_{0.50}Nb_3Se_4$ showing the $(1\bar{1}0)^*$ reciprocal lattice plane at 90 K. Diffuse superlattice spots can be seen along rows such as indicated by arrows at A. Slightly modulated lines occur on each side of the main spot rows as indicated by arrows at B.

relatively stronger up to $x = 0.75$ and there was no further change in the patterns at $x = 1.0$.

TABLE 1
Line Positions

Sample	Position, P	$1/P$	$1 - P$	$1/(1 - P)$	Host lattice spacing, c (6, 7)
$In_xNb_3Te_4$	$(0.155 \pm 0.002)c^*$	$6.45c$	$0.85c^*$	$1.18c$	3.65 Å
$In_xNb_3Se_4$	$(0.0967 \pm 0.0005)c^*$	$10.34c$	$0.90c^*$	$1.11c$	3.47 Å
$In_xNb_3S_4$	$(0.054 \pm 0.001)c^*$	$18.5c$	$0.95c^*$	$1.05c$	3.37 Å

Lines, perpendicular to **c***, similar to those noted above for the indium intercalated selenides and sulfides, have previously been reported for indium intercalated Nb_3Te_4 (8). We have never observed such lines in thallium intercalated Nb_3X_4 (X = S, Se, Te). Further, the lines have a characteristic position for each of the chalcogenides and we have not been able to detect any change in those positions as a function of temperature or composition. The distances of the lines from the main row lines is markedly different for each chalcogenide as shown in Table 1, along with further data which is considered in the Discussion.

DISCUSSION

We will first consider the possible origins of the observed SL spots and justify our conlcusion that they arise from CDW. Then, we will consider the unusual variations of the CDW vectors with composition and the surprising observation that, for certain $In_xNb_3Se_4$ samples, two sets of SL spots occurred simultaneously in the diffraction patterns. Finally, an explanation will be offered for the lines that were present in patterns from all samples with higher values of x.

Origin of SL Spots

SL spots might arise from ordering of the intercalate atoms or from CDW formation. However the spot positions, in particular the tripling of the periodicity perpendicular to the tunnels for all compositions, do not appear compatible with ordering. Also the progressive sharpening

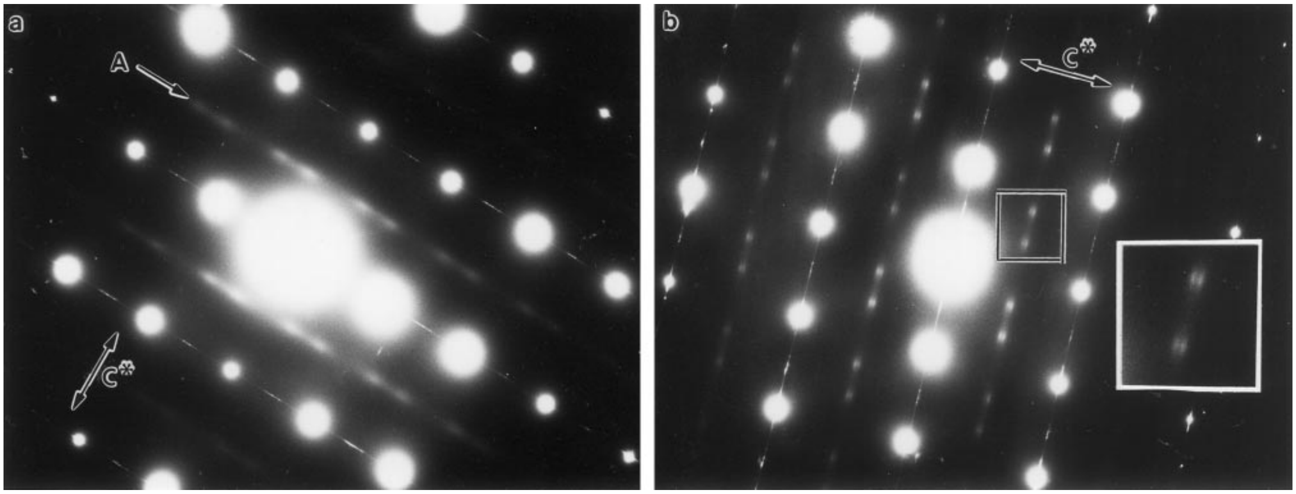

FIG. 4. Electron diffraction pattern of $In_{0.25}Nb_3S_4$ showing the $(1\bar{1}0)^*$ reciprocal lattice plane. (a) At 90 K rows of diffuse superlattice spots occurs as indicated by arrows at A. The superlattice spot pairs are not resolved. (b) At 46 K the superlattice spots are sharp and clearly resolved. The inset shows an enlargement of the area indicated.

of the spots with decreasing temperatures to 27 K would appear to require unlikely diffusion over several atomic distances. Finally, we note that the lines which were observed, together with SL spots, in samples with higher values of x are attributed to one-dimensional ordering of the indium intercalate in the tunnels. We thus conclude that ordering is an unlikely explanation of the observed SL spots, whereas the case for CDW is more convincing.

It is well known that intercalation of one- and two-dimensional crystals results in the transfer of electrons from the intercalate ions to the conduction band of the host crystal with resultant changes in the Fermi surface and the density of states at the Fermi level, $D(E_f)$. It thus appears possible that electronic conditions favorable for CDW formation could be set up in a crystal that does not exhibit such a transition in the pure state. Previously, in a discussion of the electronic band structures of Nb_3X_4 (X = S, Se, Te)-type crystals, Canadell and Whangbo (12) noted that alkali metal intercalation of the Nb_3X_4-type lattice could lead to changes in the Fermi surface nesting condition and density of states, such that interesting changes in the physical properties might ensue. So far no experimental study has been reported of their specific suggestion that alkali metal intercalates of Ti_3X_4 (X = S, Se) should be of interest. However, we note that for $K_{0.30}Ti_3S_4$ and $K_{0.26}Ti_3Se_4$ the Ti–Ti atom spacings along the chains is only very slightly less than that between the chains (14, 16, 17), so that the metal atom chains in these compounds have significantly less quasi-one-dimensional character than do the Nb atom chains in Nb_3X_4 (X = Te, Se, S). Thus, although the density of states may be favorable in the intercalated Ti_3X_4 compounds, it is unlikely that a CDW would exist. On the other hand, the intercalates of Nb_3X_4 (X = Se, S) are promising candidates for intercalation-induced CDW because, even though the calculated band structures and Fermi surfaces of all three compounds are similar (10, 11), the telluride is the only member of the family that exhibits a CDW below room temperature. The CDW interpretation of the SL spots in the intercalated selenides and sulfides is strengthened by the fact that the positions of these spots are given by an equation of the same form as that which describes the SL spot positions in pure Nb_3Te_4. The structural and electronic effects of intercalation for various transition metal chalcogenide tunnel structures have been studied in considerable detail by Bensch and co-workers (13, 17–20). Although the host–intercalate interactions are complex and not well understood, several general features have emerged. Based on single-crystal X-ray analysis of a number of intercalated isostructural M_3X_4 (M = T, V, Nb; X = S, Se, Te) compounds, the structure of the host lattice was found to be largely undisturbed by intercalation, independent of the nature of the guest ions. However, the ratio of the interchain metal–metal atom separation to the intrachain separation was shown to correlate with the valence electron concentration (VEC) per chain metal atom (20). Effectively, the intrachain separations remain essentially unchanged, while the interchain Nb atom separation are increased by the introduction of the intercalate. These changes are hardly reflected in the measured lattice parameters, since only small shifts of the metal atoms within the chalcogenide framework are involved. Within a simple rigid band picture, the VEC is directly proportional to the intercalate concentration. Although no structural data is currently available for intercalates of Nb_3Se_4 or Nb_3S_4, a similar correlation is likely and, as a result, intercalation of these compounds would be expected to favor CDW formation by accentuating the one-dimensional characteristic of the Nb atom zigzag chains.

Finally, we note that the SL spots and lines previously reported for $In_xNb_3Te_4$ (8) are very similar to those reported here for the selenides and sulfides. Previous resistivity results on polycrystalline $In_xNb_3Te_4$ by Ohtani *et al.* (21) showed that typical CDW anomalies occurred at temperatures where the SL spots first appeared. These authors also studied resistivity of indium intercalated Nb_3Se_4 and Nb_3S_4 and the only anomaly they observed was a sharp resistivity rise for $In_xNb_3Se_4$ ($x \geq 0.40$) at 45 K. However, we note that their resistivity measurements started at 273 K, while we observed very diffuse SL spots for both the selenides and sulfides at room temperature, indicating that the CDW were already present, although very weakly correlated. We have not observed any changes in the diffraction patterns of $In_xNb_3Se_4$ associated with the resistivity rise at 45 K reported by Ohtani *et al.* (21). We conclude that the association of the superlattices observed in the selenides and sulfides with CDW is the most reasonable interpretation, and the gradual sharpening of the spots on cooling below room temperature is a reflection of improving correlation of the CDW both along and perpendicular to the tunnel directions.

Variation of the Wave Vectors

Although the appearance of CDW in Nb_3X_4 (X = Se, S) is not unexpected, as discussed above, the variation of the wave vectors with composition was surprising and was not compatible with a simple increase in the Fermi energy as electrons were progressively transferred from the intercalate atoms to the conduction band. The changes of the wave vectors, $\mathbf{q}_c$, with intercalate content, x, are similar for the selenides and sulfides but there are differences in detail. Thus, for the first detected SL spots ($x = 0.2$) $\mathbf{q}_c$ is about 0.41 for the selenide and 0.47 for the sulfide. With increasing x, both vectors increase to a value approaching 0.5 and then decrease to $\mathbf{q}_c = 0.31$ for Nb_3Se_4 and $\mathbf{q}_c = 0.21$ for Nb_3S_4 One cannot tell from the diffraction patterns if the wave vector should be taken as the shorter distance from the main spot to a SL spot or, alternatively, as one minus this distance, but in the above data we have chosen the smaller values of $\mathbf{q}_c$ in all cases. If the assumption is made that the tunnels are uniformly and progressively filled as x increases, then one must also expect that the Fermi energy and the wave vectors would uniformly increase. In this case, after reaching the value near 0.5, $\mathbf{q}_c$ would be expected to keep increasing and the larger of the two possible values for $\mathbf{q}_c$ should be chosen. The final results would be $\mathbf{q}_c = 0.69$ for Nb_3Se_4 and 0.79 for Nb_3S_4. These values are unacceptable, as they represent increases of almost 70% over the initially observed vectors and one can deduce from the density of states curves (11, 12) that a shift of this magnitude in the Fermi energy is not compatible with the number of electrons donated by the intercalate, even assuming that the indium were in a triply ionized state. We thus conclude that the smaller values of $\mathbf{q}_c$ must be chosen in every case and consider the possibility that the tunnels are not uniformly filled. A plausible scenario is that some fraction of the tunnels, in an ordered arrangement, initially begin to be filled preferentially with intercalate atoms. For instance, if 2/3 of the tunnels were occupied, the zigzag Nb atom chains, which are crystallographically identical in the pure material, would be divided into two sets with different surroundings of filled tunnels. Thus, two sets of columns would occur in the crystals with one set being preferentially surrounded by occupied tunnels and expected to receive a majority of the transferred electrons. The effect on the Fermi surface would be complicated, because it has been shown that pure Nb_3X_4 already has three sets of Fermi surfaces, each made up of undulating plane sheets perpendicular to the chains, associated with the three niobium chains in the unit cell (11, 12). We suggest that one of these surfaces is modified by the intercalate in such a way that it becomes conducive for CDW formation. It is possible that the screening effect of the In ions in the tunnels would result in a flatter Fermi surface with significant nesting areas. With progressive filling of the tunnels the Fermi energy would shift to higher energy values and hence account for the observed initial increases in the CDW vectors. For compositions x greater than about 0.4, we suggest that intercalate atoms are forced into all of the tunnels, so that electrons are transferred uniformly to all niobium chain columns and the CDW vectors decrease and approach a fixed value for $x > 0.5$. The decrease in the wave vectors associated with the change from partial to complete occupancy of the tunnels would result from the partially filled tunnels being able to accommodate a larger proportion of intercalate atoms than can be accommodated when all tunnels are occupied. However, another possibility is that the In may be in a higher valence state initially, when only some tunnels are occupied, and subsequently change to an ionization of +1 when all the tunnels are occupied. There is evidence that a similar valence shift can occur in the intercalated tunnel structure $Tl_xV_5S_8$, which was studied using NMR methods by Schramm and Schollhorn (22). These workers deduced that the Tl changed from an oxidation state of +3 to +1 as the composition x increased.

Two Sets of SL Spots from the Same Crystal

For $In_xNb_3Se_4$ with $x = 0.33$ and 0.40 we have observed two sets of SL spots at 90 K; for the former composition, $\mathbf{q}_{c1} = 0.425 \pm 0.001$ and $\mathbf{q}_{c2} = 0.39 \pm 0.01$ while for the latter $\mathbf{q}_{c1} = 0.425 \pm 0.001$ and $\mathbf{q}_{c2} = 0.333 \pm 0.003$. The $\mathbf{q}_{c1}$ spots are sharper in both cases, while the $\mathbf{q}_{c2}$ spots are more diffuse. On cooling to 27 K the diffuse spots become sharper. This occurrence of two sets of SL spots brings to mind the well-known case of $NbSe_3$, where two sets of SL spots associated with two CDW are observed below 58 K. These two CDW are attributed to nesting between two sets of Fermi surfaces which arise from two distinct prismatic columns in the unit cell (23). It is tempting to invoke a similar effect to account for the appearance of two sets of SL spots in $In_xNb_3Se_4$ Here, in contrast to the situation in $NbSe_3$, the environments of all the Nb zigzag chains in the host structure are identical. However, the three chains per unit cell result in three bands crossing the Fermi level and give rise to three independent Fermi surfaces (10, 11). Since anomalies in the electrical resistivity and magnetic susceptibility of Nb_3Te_4 are known to occur at about 100 and 40 K (15), it is possible in principle to attribute both anomalies to CDW associated with nesting of distinct pairs of Fermi surfaces. Sakai *et al.* (24), in an earlier study of Li intercalation in Nb_3Te_4, found that the higher temperature anomaly was progressively suppressed while the lower temperature anomaly increased as a function of intercalate concentration. These workers suggested that the intercalate modified the characteristics of the Fermi surfaces independently, reducing and increasing the nesting areas for the upper and lower anomalies, respectively. It is significant, however, that no experimental evidence for a periodic structural distortion accompanying the lower temperature anomaly in Nb_3Te_4 or related intercalates has been reported, despite several attempts to observe associated diffraction effects (15). Thus, we consider it unlikely that such a mechanism could account for the occurrence of two sets of SL reflections observed at 90 K in the $In_xNb_3Se_4$ compounds. Alternatively, we suggest that the preferential filling of some tunnels leads to two electronically distinct sets of Nb atom chains, which give rise to two sets of Fermi surfaces and two CDW. As the composition x increases beyond 0.4, the $\mathbf{q}_{c1}$ spots disappear and the $\mathbf{q}_{c2}$ spots shift to a final value of $\mathbf{q}_{c1} = 0.311 \pm 0.003$ at $x = 0.50$. At the same time lines appear in the diffraction patterns lying perpendicular to the tunnel axis. We believe that this state, which occurs for $x \geq 0.5$, is characterized by a uniform occupancy of all tunnels. We have not observed two sets of CDW spots for any of the sulfide specimens but it is possible that this effect might occur over a very limited composition range that we did not examine.

Lines Perpendicular to the Tunnel Axes

Lines are observed on both sides of the main spot rows, lying perpendicular to **c***, in diffraction patterns of $In_xNb_3Se_4$ and $In_xNb_3S_4$ for $x \geq 0.5$. These lines are slightly broadened at 90 K but become sharp at 27 K. Similar lines have previously been reported for $In_xNb_3Te_4$ (8). In all cases the positions of the lines are independent of temperature within experimental error but the positions vary markedly for the telluride, selenide, and sulfide as listed in Table 1. It is also shown in Table 1 that the distances, P, of the lines from the main rows correspond to several unit cell distances in the crystal, which does not appear to be related to physical reality. We therefore take the spacings $(1 - P)$, which in each case inverts to a value that is slightly larger than **c**, the unit cell distances along the tunnels. These lines are due to planes of scattering in reciprocal space. Following Bronsema and Mahy (25), who observed similar lines at incommensurate positions in electron diffraction patterns of a different intercalated tunnel structure, $K_xV_5S_8$ $(x > 0.5)$, we attribute this scattering to In ions which are ordered in the tunnels, with practically no interaction between the ions in adjacent tunnels. This lack of interaction is not surprising since the tunnel separations are about 10 Å and there are screening effects due to the intermediate chalcogen and Nb ions. An occupation probability function of the ions on the available sites could then give rise to the observed incommensurate line positions. It appears that, on average, the In ions require slightly more than one unit cell distance. We note that the modulation distance increases with the crystal **c** spacing, indicating that the In lattice sites play a role.

We have demonstrated that CDW can be induced, by indium intercalation, in inorganic tunnel structures that do not exhibit such phenomena in the pure state. The surprising variations of the CDW characteristics with composition highlights the striking new possibilities that such compounds exhibit to experimentally investigate the poorly understood area of CDW/intercalate ion/lattice interactions. The model proposed above accounts qualitatively for the rather complex effects of In intercalation in Nb_3Se_4 and Nb_3S_4, but we have no direct experimental evidence for the initial preferential filling of a partial set of the tunnels. It should be possible, using high-resolution electron microscopy through specimens cut perpendicular to the fiber axis, to determine whether the tunnels are filled preferentially for the lower indium concentrations. We have initiated such experiments, as well as transport measurements on these compounds.

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