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# Influence of niobium on the charge-density-wave transition of $Ni(Ta_{1-x}Nb_x)_2Se_7$

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The influence of doping by niobium on the low-temperature charge-density-wave (CDW) state of $NiTa_2Se_7$ has been investigated by x-ray diffraction and measurements of the electrical conductivity. Doping concentrations in $Ni(Ta_{1-x}Nb_x)_2Se_7$ varied between 0.5% and 30%. X-ray crystal structure refinements showed that the niobium atoms statistically replace the tantalum atoms, but with a ratio of 2:1 for the two crystallographically independent tantalum sites Ta1 and Ta2. Niobium was not found on the Ni sites nor intercalated between the layers. Previous investigations have established that the primary CDW is located on the Ni and Se2 atoms, and only a small influence on the CDW was expected from Nb doping of the Ta chains. Nevertheless, we found that the CDW was very sensitive to the level of doping $x$ with $dt_c/dx=-16$, where $t_c=T_c(x)/T_c(0)$ is the reduced transition temperature. Similar values for $dt_c/dx$ were calculated for different isoelectronically doped compounds with transition temperatures varying between $T_c=59\,\mathrm{K}$ ($NbSe_3$) and 263 K [$(TaSe_4)_2I$]. It is suggested that this can be explained by a common mechanism of weak pinning of the CDW to the impurities. The results are rationalized by considering the recently found $4k_F$ component of the CDW, which is located on the Ta2 atoms. The large effects of doping on the CDW transition can then be understood in terms of the effect of doping on the $4k_F$ CDW and the interactions between the primary CDW and the $4k_F$ CDW.

## I. INTRODUCTION

The structure and physical properties of charge-density-wave (CDW) compounds have been investigated for many years.[1–3] The interest concentrates on improving our understanding of the physics of one-dimensional (1D) systems, and on possible applications of the nonlinear conductivity of these materials. Impurities or doping provide pinning centers for the CDW. They are responsible for modified electrical transport properties, e.g., an increased threshold field for the CDW contribution to the charge transport, and they may lead to suppression of the CDW transition. Systematic investigations of these effects have been performed mainly for $NbSe_3$.[3–5] Extensive theoretical studies have been made and different models for the influence of impurities on the transport properties have been developed.[6,7] On the other hand, only a few studies have investigated the influence of the impurity concentration on the critical temperature of the Peierls transition [e.g., for $(Nb_{1-x}Ta_x)Se_3$,[8] $(Ta_{1-x}Nb_xSe_4)_2I$,[9] and $K_{0.3}(Mo_{1-x}W_x)O_3$ (Ref. 10)]. Furthermore, in only one investigation was an attempt made to determine the crystal structure of the doped compounds and to determine the positions of the dopant atoms.[11] In the present paper we report on the distribution of niobium in doped $Ni(Ta_{1-x}Nb_x)_2Se_7$ and on the influence of the dopant on the CDW transition of this compound.

$NiTa_2Se_7$ crystallizes in the monoclinic space group $C2/m$ with lattice parameters $a=13.83\,\text{Å}$, $b=3.48\,\text{Å}$, $c=18.58\,\text{Å}$, and $\beta=108.8°$ at $T=123\,\mathrm{K}$.[12] The structure is characterized by chains of Ni atoms and two crystallographically independent chains of Ta atoms. The Ta1 chain has Ta atoms in trigonal prismatic coordination by Se similar to the structure of the chains in $NbSe_3$. Both the Ni and Ta2 chains have the metal atom in a distorted octahedral coordination by Se (Fig. 1). An incommensurate CDW with a wave vector of $\vec{q}=(0,0.483,0)$ has been found to develop below a transition temperature of $T_c=53\,\mathrm{K}$.[13]

The principal part of the modulated structure corresponds to first-order harmonic displacements of the atoms ($2k_F$ CDW), which were determined from the measured intensities of the first-order satellite reflections.[14] The principal distortions were found to be transverse displacements of the Ni, and Se2 atoms. This already sets $NiTa_2Se_7$ apart from other CDW compounds, because a true 1D character would require a longitudinal displacement wave. The latter is what has been found in, for example, $NbSe_3$.[15] In a study parallel to the present one, we have determined the modulated structure of $NiTa_2Se_7$ including the second-order satellites in x-ray scattering and the second harmonics of the displacement wave ($4k_F$ CDW).[16] Whereas the transverse modulation of Ni and Se2 was confirmed for the $2k_F$ CDW, the principal part of the $4k_F$ CDW was found to involve a longitudinal

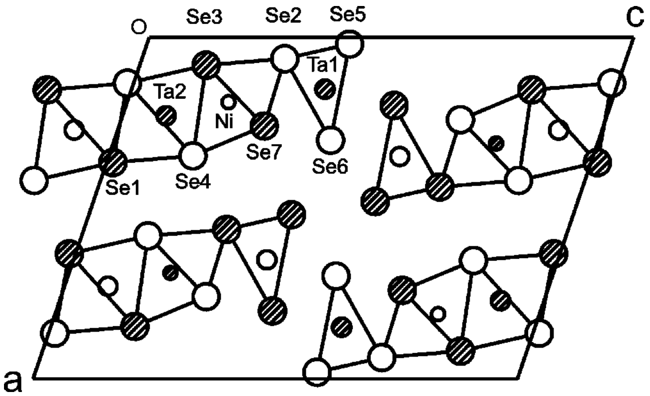

FIG. 1. Projection of one unit cell of the basic structure of $Ni(Ta_{1-x}Nb_x)_2Se_7$ parallel to the (*a*,*c*) plane. Open circles represent atomic positions at $y=0.5$, hatched circles at $y=0.0$.

TABLE I. Results of the structure refinement of Ni$(\mathrm{Ta}_{1-x}\mathrm{Nb}_x)_2\mathrm{Se}_7$ with $x=10\%$. For each crystallographically independent atom the relative coordinates (*x,y,z*) are given as well as the components of the temperature tensor ($U_{ij}$ in Å$^2$).

| Atom | Occupancy | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{13}$ |
|---|---|---|---|---|---|---|---|---|
| Ta1 | 0.846(6) | 0.151 58(2) | 0.0 | 0.399 18(2) | 0.0080(1) | 0.0060(1) | 0.0105(1) | 0.0034(1) |
| Nb1 | 0.154 | 0.151 58 | 0.0 | 0.399 18 | 0.0080 | 0.006 | 0.0105 | 0.0034 |
| Ta2 | 0.940(6) | 0.228 98(3) | 0.0 | 0.089 23(2) | 0.0114(1) | 0.0122(1) | 0.0142(1) | 0.0058(1) |
| Nb2 | 0.060 | 0.228 98 | 0.0 | 0.089 23 | 0.0114 | 0.0122 | 0.0142 | 0.0058 |
| Ni | 1.000(20) | 0.190 41(9) | 0.5 | 0.209 39(7) | 0.0122(4) | 0.0077(4) | 0.0145(4) | 0.0016(3) |
| Nb3 | 0.000 | 0.190 41 | 0.5 | 0.209 39 | 0.0122 | 0.0077 | 0.0145 | 0.0016 |
| Se1 | 1.000 | 0.366 60(6) | 0.0 | 0.012 98(5) | 0.0101(3) | 0.0081(3) | 0.0122(3) | 0.0040(2) |
| Se2 | 1.000 | 0.062 12(8) | 0.5 | 0.295 03(6) | 0.0166(3) | 0.0077(3) | 0.0157(3) | −0.0036(3) |
| Se3 | 1.000 | 0.082 11(6) | 0.0 | 0.137 58(5) | 0.0092(3) | 0.0088(3) | 0.0146(3) | 0.0049(2) |
| Se4 | 1.000 | 0.346 35(7) | 0.5 | 0.173 05(5) | 0.0103(3) | 0.0086(3) | 0.0144(3) | 0.0031(2) |
| Se5 | 1.000 | 0.019 54(6) | 0.5 | 0.418 13(5) | 0.0096(3) | 0.0081(3) | 0.0171(3) | 0.0069(2) |
| Se6 | 1.000 | 0.301 33(6) | 0.5 | 0.446 77(5) | 0.0079(2) | 0.0062(3) | 0.0199(3) | 0.0033(2) |
| Se7 | 1.000 | 0.259 56(60 | 0.0 | 0.299 83(5) | 0.0102(3) | 0.0084(3) | 0.0120(3) | 0.0043(2) |

modulation of Ta2. It was concluded that $\mathrm{NiTa_2Se_7}$ supports independent $2k_F$ and $4k_F$ CDW's.[16]

The goal of the present study is to improve the understanding of the effect of impurities on the CDW state. Doping by niobium was chosen because Nb is isoelectronic with Ta. Furthermore, Nb and Ta atoms are of similar size. This implies that the band filling of the pristine and doped compounds will be the same and that strain due to doping can be neglected. Because the primary CDW is located on Ni and Se2 chains, a small effect of the doping on the CDW was expected, allowing crystallographic studies of highly doped compounds in the CDW state. We will show that indeed Nb replaces only Ta in the doped compounds, but in contradiction with the expectations we have also found that the CDW transition is extremely sensitive to doping, with the CDW transition disappearing for $x > 2.5\%$. An attempt is made to understand these features by considering the interactions between the $2k_F$ and $4k_F$ CDW's. A universal behavior of the doping dependence of the reduced transition temperature $dt_c/dx$ with $t_c(x) = T_c(x)/T_c(0)$ was found.

## II. DISTRIBUTION OF NIOBIUM IN Ni$(\mathrm{Ta}_{1-x}\mathrm{Nb}_x)_2\mathrm{Se}_7$

Ni$(\mathrm{Ta}_{1-x}\mathrm{Nb}_x)_2\mathrm{Se}_7$ crystals were grown by gas transport in evacuated quartz ampoules starting with the elements in the correct ratio.[12] Samples were made with doping concentrations *x* between 0.5% and 30%. In all cases thin, needle-shaped crystals were obtained after a period of about 7 days. Inspection by optical microscopy showed that less doping gave larger single crystals of better quality. This was confirmed by the x-ray scattering experiments, which gave narrower reflection profiles for the less doped samples.

The amount and sites of the Nb atoms were obtained from complete structure refinements against x-ray scattering data on selected single crystals from the batches with $x = 2.5\%$, 10%, 20%, and 30%. All diffraction experiments were performed at room temperature on a Nonius MACH3/CAD4 diffractometer with Mo $K\alpha$ radiation from a rotating-anode x-ray source ($\lambda = 0.710\,73$ Å). The samples were chosen rather small with a maximum diameter of the needles of 0.02 mm in order to reduce absorption. The length of the samples exceeded in all cases the diameter of the incident x-ray beam. For all samples, lattice parameters were determined from the setting angles of 25 reflections in the range $18° < \Theta < 20°$. For $x = 0.1$ they were obtained as $a = 13.8626(11)$ Å, $b = 3.4921(4)$ Å, $c = 18.6391(18)$ Å, and $\beta = 108.905(8)°$. The lattice parameters were slightly larger than the values obtained by Sunshine and Ibers,[12] which can be attributed to the different temperatures of the measurement. The lattice parameters do not depend significantly on the concentration of the doping. This confirms the general observation that Nb and Ta have the same size in their respective compounds.

For all samples integrated intensities were measured for a half sphere in reciprocal space in the range $2° < \Theta < 35°$. For the samples with $x = 2.5\%$ and 10% the measurement was extended to reflections with $\Theta < 45°$, in order to achieve a better accuracy for the determination of such low doping concentrations. For all data sets Lorentz and polarization corrections were applied using the program HELENA.[17] Special care was taken to correct the measured intensities for absorption ($\mu = 293.1\ \mathrm{cm}^{-1}$). The shapes of the crystals were refined from $\psi$ scans of several reflections with the computer program HABITUS.[18] These shapes were then used to compute transmission coefficients for all reflections of each sample, and the data were corrected for absorption accordingly. Structure refinements were performed with JANA98.[19]

All data sets could be fitted reasonably well with the structure of $\mathrm{NiTa_2Se_7}$. Improvements of the fits were obtained by the introduction of Nb, and the positions and concentrations of Nb in the different samples were thus determined. Both Ta and Ni were replaced partly by Nb. The occupation fractions of Nb on the Ta1, Ta2, and Ni sites were varied independently, while keeping the occupation of each site equal to 1. Furthermore, the position and temperature factors of the Nb atoms were restricted to the values of the atom it replaced. The complete refined structure model for the crystal with a doping concentration of 10% is given in Table I. It is found that the coordinates of the atoms are not affected by the presence of niobium. The total amount of

TABLE II. X-ray diffraction results for the doped $Ni(Ta_{1-x}Nb_x)_2Se_7$ samples.

| $x$ | 0.025 | 0.1 | 0.2 | 0.3 |
|---|---|---|---|---|
| No. of reflections measured | 4293 | 3867 | 1827 | 1411 |
| No. of reflections observed | 3363 | 3200 | 1319 | 1025 |
| $R$ | 0.037 | 0.044 | 0.079 | 0.075 |
| $R_W$ | 0.045 | 0.050 | 0.092 | 0.095 |
| Occupation of Nb1 | 0.003(3) | 0.077(3) | 0.103(5) | 0.195(5) |
| Occupation of Nb2 | 0.06(4) | 0.030(3) | 0.036(5) | 0.065(5) |
| Total Nb content | 0.009(7) | 0.107(6) | 0.139(9) | 0.26(1) |

niobium as determined by the refinement is obtained as $x = 10.7(0.5)\%$. Within the experimental errors this is equal to the nominal amount of 10%. This result clearly shows that the Ta1 site contains twice as much niobium as the Ta2 site does. No significant amount of Nb was found on the Ni site. A difference Fourier map did not give evidence for atoms at intercalated positions. It was thus concluded that Nb is incorporated into the structure by replacing Ta only.

Similar conclusions were reached for the other samples. The results of the different refinements are summarized in Table II and Fig. 2. For the lowest amounts of doping the agreement between observed and calculated structure factors is excellent, whereas for the higher amounts of doping just a good agreement could be obtained. The latter fact again illustrates the poorer quality of the crystals of the higher-doped compounds. It is an indication that these samples will be affected by disorder, for example, in the packing of the layers. For doping concentrations $x$ below 2.5% the accuracy of the refinement was not sufficient to determine significant values of the site occupancies of niobium. For all doping concentrations the total amount of Nb in the compound determined by refinement was close to the initial doping concentration of the synthesis. In particular, enrichment of Nb was not observed even for low doping concentrations.

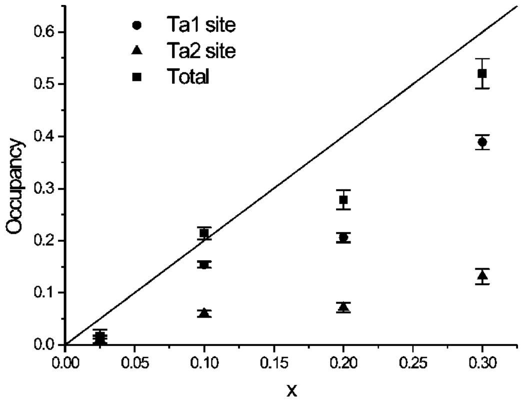

FIG. 2. Distribution of the niobium atoms within the structure of $Ni(Ta_{1-x}Nb_x)_2Se_7$ for various doping concentrations between $x = 2.5\%$ and 30%. Circles represent the occupation of the Ta1 site, triangles the occupation of the Ta2 site. The error bars give the standard deviations of the refinement only. Squares indicate the total measured concentration as a function of the given doping. These values lie close to the ideal values, which are indicated by the straight line. No significant amount of Nb was found on the Ni site.

## III. ELECTRICAL CONDUCTIVITY OF NIOBIUM-DOPED $NiTa_2Se_7$

Crystals of a few millimeters to 1 cm long were selected for the measurements of the electrical conductivity. Four gold contacts of 0.2 mm width were evaporated onto the needle-shaped crystals at distances of 0.5 mm apart. The dc conductivity was measured with the four-probe method, using the two outermost contacts as current contacts the two innermost contacts to measure the voltage drop. Due to the shape of the crystals and the arrangement of the contacts, the conductivity could be measured only along the needle direction, which coincides with the direction of the chains ($\vec{b}$ axis). The electrical conductivity between 5 and 300 K was measured in a liquid-He cryostat for an undoped sample and for samples with doping concentrations of 0.5%, 1%, 1.75%, 2.5%, and 10%. The results are shown in Fig. 3. The transition temperatures toward the CDW state were determined from the onset of the anomaly in the resistance versus temperature curves. They are summarized in Fig. 4. Anomalies in the temperature dependence of the resistance could not be identified in the sample with $x = 0.1$.

The CDW transition of the pure compound ($x = 0$) is found to occur at $T_c = 63.0\,\mathrm{K}$. This value is about 10 K higher than that previously reported for $NiTa_2Se_7$.[13] The temperatures in our experiments were calibrated by standard procedures. Furthermore, they were checked by measuring the conductivity of a $NbSe_3$ single crystal. Anomalies were observed at $T = 143$ and 59 K. These values are equal to the respective values of the transition temperatures as published for the two CDW transitions of $NbSe_3$.[20] Therefore, the val-

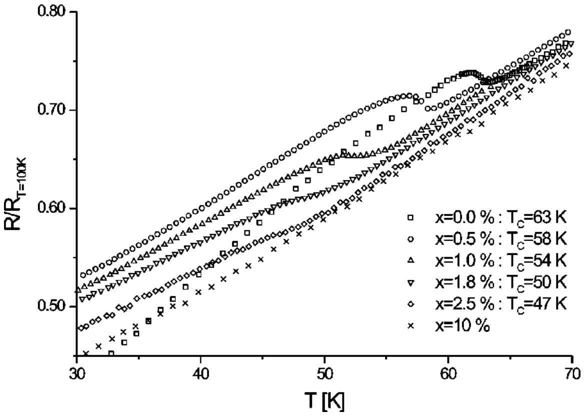

FIG. 3. Normalized resistance versus temperature for doping concentrations between $x = 0.0\%$ and 10%.

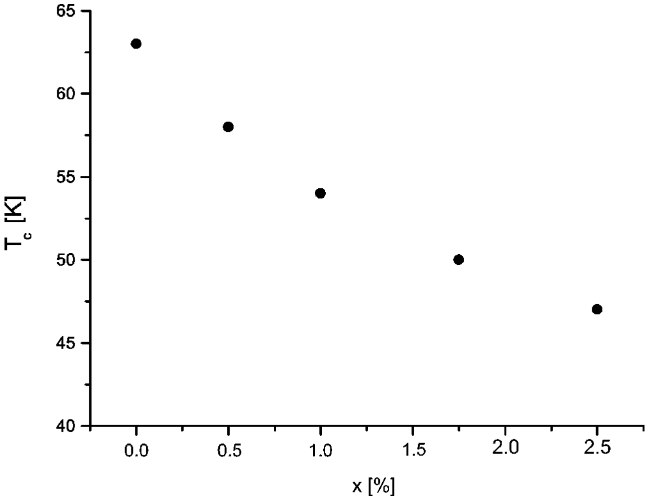

FIG. 4. Transition temperature to the CDW state as a function of doping concentration $x$ determined from the resistivity data.

ues for the temperatures in the present experiments are correct on an absolute scale to within at least 1 K. The difference between the values for $T_c$ of NiTa$_2$Se$_7$ as reported in Ref. 13 and as presently observed is attributed to a better quality of our crystals and to a lower concentration of impurities in our crystals. The latter explanation is supported by the observation that a concentration of 1% Nb is sufficient to lower the transition temperature by about 10 K.

The second feature obvious from Fig. 3 is that for increasing amounts of doping the transitions appear less pronounced. Above $T_c$ the temperature dependences of the resistance are nearly equal for the different samples. Below $T_c$ the slopes of the resistance versus temperature curves decrease for increased amounts of doping, and changes in the slope occur over a larger temperature interval. This indicates a broadening of the region where transition effects occur.

## IV. DISCUSSION

We have found a strong influence of isoelectronic doping on the CDW in NiTa$_2$Se$_7$. With $x$ being the fraction of Ta replaced by Nb, we find a reduction of the reduced transition temperature $t_c(x)=T_c(x)/T_c(0)$ equal to $dt_c(x)/dx=-15.9$ in the limit $x\rightarrow 0$. The effect of the transition on the electrical conductivity becomes smaller for increased amounts of doping, such that the transition becomes invisible for $x\gtrsim 2.5\%$. For high doping concentrations the samples remain metallic, as can be seen in the resistivity curve for $x=10\%$.

These features are similar to what has been found from resistivity data for other quasi-1D CDW compounds with isoelectronic doping [for the low-temperature CDW transition of (Nb$_{1-x}$Ta$_x$)Se$_3$,[8] for (Ta$_{1-x}$Nb$_x$Se$_4$)$_2$I,[9] and for the tungsten-doped blue bronze K$_{0.3}$(Mo$_{1-x}$W$_x$)O$_3$ (Ref. 10).] We have computed $dt_c(x)/dx(x\rightarrow 0)$ for these compounds from conductivity data published in the literature (Table III). Within the estimated errors a single value is found for all compounds. This indicates the same mechanism for the dependence of $T_c$ on the concentration of the dopant. Furthermore, the coincidence of $dt_c(x)/dx$ for isolectronically doped CDW systems suggests that this value is a universal constant depending only on the pinning mechanism of the CDW. Further theoretical work is highly desirable to understand this property of doped CDW compounds that has been overlooked so far.

TABLE III. $dt_c(x)/dx$ of the reduced transition temperature $t_c=T_c(x)/T_c(0)$ as derived from conductivity data of the present study [Ni(Ta$_{1-x}$Nb$_x$)$_2$Se$_7$] and from data published in the literature for the low-temperature transition of (Nb$_{1-x}$Ta$_x$)Se$_3$ (Ref. 8), for Ta$_{1-x}$Nb$_x$Se$_4$)$_2$I (Ref. 9), and for the tungsten-doped blue bronze K$_{0.3}$(Mo$_{1-x}$W$_x$)Oh$_3$ (Ref. 10).

| Compound | $dt_c(x)/dx$ |
|---|---|
| Ni(Ta$_{1-x}$Nb$_x$)$_2$Se$_7$ | $-16$ |
| (Nb$_{1-x}$Ta$_x$)Se$_3$ | $-15$ |
| (Ta$_{1-x}$Nb$_x$Se$_4$)$_2$I | $-20$ |
| K$_{0.3}$(Mo$_{1-x}$W$_x$)O$_3$ | $-16$ |

In Nb$_{1-x}$Ta$_x$Se$_3$ even small amounts of Ta ($x<0.01$) were shown to result in a loss of long-range order of the CDW and breaking up of the CDW into domains of finite size. The widths and integrated intensities of Bragg reflections indicated that both the domain size and the amplitudes of the atomic displacements decreased for increased amounts of doping.[3,21] This reduction of the CDW amplitude matches our observation of a reduced effect of the CDW transition on the electrical conductivity. In accordance with our results, NbSe$_3$ remained metallic for isoelectronic doping and high doping concentrations.[1]

In all compounds except Ni(Ta$_{1-x}$Nb$_x$)$_2$Se$_7$ the dopant replaces atoms in the chains carrying the CDW. The large effect on the CDW can be explained by the influence of these atoms on the electronic band, and their role as centers for pinning and scattering. Alternatively, partial replacement of atoms that are not involved in the quasi-1D system carrying the CDW has been found to have little effect on the CDW properties. For example, in (K$_{1-x}A_x$)$_{0.3}$MoO$_3$ ($A=$Na, Rb) hardly any influence of doping was observed on the width of the Bragg reflections and on the value of $T_c$, for concentrations up to $x=50\%$.[22,24]

In the case of Ni(Ta$_{1-x}$Nb$_x$)$_2$Se$_7$ the primary CDW has been shown to reside on the Ni and Se2 atoms.[14] The substitution of Nb for Ta replaces atoms of the chains that are not involved in the primary CDW. Nevertheless, a large effect is observed on the CDW properties. A straightforward interpretation in terms of scattering centers in the CDW-carrying chains is no longer valid. Instead, we believe that the unusual behavior of Ni(Ta$_{1-x}$Nb$_x$)$_2$Se$_7$ can be attributed to the interactions between the primary CDW and a secondary CDW on the Ta2 chain. Our recent refinement of the modulated structure showed that the primary $2k_F$ CDW involves the Se2 and Ni atoms, while a $4k_F$ CDW originates on the Ta2 chains.[16] It was concluded that there are independent $2k_F$ and $4k_F$ CDW's residing in different parts of the structure. This conclusion was supported by electronic band structure calculations,[23] which suggested nesting properties of the Fermi surface for the electronic subbands of the Ta2 chain and the Se chains.

However, truly independent CDW's should have independent wave vectors. The observed relation $4k_F=2\times 2k_F$ is possible only when interactions between the two CDW's are

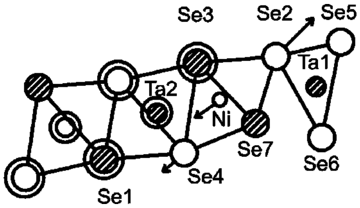

FIG. 5. Distortion pattern of the low-temperature CDW phase as determined in Ref. 16. Arrows indicate the modulation amplitudes of the $q$ distortion parallel to the $(a,c)$ plane. Circles indicate $2q$ distortion parallel to the $b$ direction.

assumed. This might occur due to the amplitudes of both CDW's on the atom Se3, and the small observed amplitude of the primary CDW on Ta2 (Fig. 5),[16] but a detailed understanding of the coupling mechanism has not yet been achieved. $NiTa_2Se_7$ is the only inorganic CDW compound for which a $2k_F$ and a $4k_F$ CDW have been found. Up to now this feature was observed only in organic CDW compounds like tetrafluoro-tetracyanoquinodimethane TTF-TCNQ,[25] where strong electronic correlations have been suggested to cause this behavior. The observation that CDW fluctuations of both the $2k_F$ and $4k_F$ CDW's persist well above $T_c$[13] shows that the interactions between the two CDW's are already important near $T_c$. In analogy with the observations for other CDW compounds, doping at the Ta2 atom positions will destroy the long-range order of the CDW on the Ta2 chains. The coupling of the two CDW's will lead to similar effects on the primary CDW. Lowering of $T_c$ and a reduction of the amplitude thus results for both CDW's even though doping affects the chains responsible for the $4k_F$ CDW only.

Our data do not give direct information on the mechanism that destroys the secondary CDW on the Ta atoms. The observation that the values of $dt_c(x)/dx$ are indeed similar for $Ni(Ta_{1-x}Nb_x)_2Se_7$ and $(Nb_{1-x}Ta_x)Se_3$ (Table III) leads to the conclusion that the pinning mechanism caused by the dopant is identical in both cases. For the isoelectronic doping of $NbSe_3$ with Ta weak pinning has been observed.[3,5]

## V. CONCLUSIONS

We have determined that in doped $Ni(Ta_{1-x}Nb_x)_2Se_7$ the Nb atoms partially replace the two crystallographically independent Ta atoms in the ratio 2:1. Both $T_c$ and the CDW amplitude decreased rapidly upon doping, and they disappear entirely for concentrations just above 2.5% as determined by conductivity measurements. The explanation for these observations is the interaction between the primary $2k_F$ CDW and the secondary $4k_F$ CDW residing on the Ta2 chain. The doping dependence of the reduced transition temperature $dt_c/dx$ for $Ni(Ta_{1-x}Nb_x)_2Se_7$ was found to be similar to values computed for other isoelectronically doped compounds from data in the literature. Therefore it is assumed that the dopant in $Ni(Ta_{1-x}Nb_x)_2Se_7$ causes weak pinning of the $4k_F$ CDW. The value of $dt_c/dx$ has been found as a universal constant depending only on the pinning mechanism of the CDW.

$Ni(Ta_{1-x}Nb_x)_2Se_7$ is the first compound to our knowledge where the primary CDW can be destroyed by doping of sites next to the chain responsible for the primary CDW. Further x-ray diffraction studies are desirable to get a more detailed view of the interactions of the two chains. It will be particularly interesting to study the structural change of the $2k_F$ and $4k_F$ CDW's caused by doping. Similar behavior of the intensities of the satellite reflections corresponding to the two waves would be a clear indication for the model described above.

For $NbSe_3$ x-ray scattering at temperatures well below $T_c = 144$ K has shown that the second-order satellite reflections of the $\vec{q}^{\,1}$-type CDW have intensities up to about 5% of the $2k_F$ scattering.[26] Up to now, this scattering has not been considered in studies concerned with the structure of the CDW and with the effects of doping on the properties of the CDW. It would be interesting to determine, for example, whether the $2\vec{q}^{\,1}$ scattering corresponds to a squaring of the $\vec{q}^{\,1}$-type CDW or represents an independent CDW in $NbSe_3$ similar to the $4k_F$CDW observed in $NiTa_2Se_7$. This is of particular interest because $NbSe_3$ already possesses two CDW's on different chains at low temperatures.[27] The two CDW's are in this case coupled by Coulomb interactions although the two wave vectors remain in an incommensurate relationship.[28]

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