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X-ray investigation of the q_1 charge-density-wave modulation in substituted Ti- and Ta-NbSe$_3$

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We present an x-ray diffuse scattering study of the perturbation of the charge-density-wave structure by impurities in doped NbSe$_3$. Substitution of the transition-metal element niobium is performed either by an isoelectronic impurity, tantalum, or by a nonisoelectronic impurity, titanium, with the concentration equal to $x=2\%$ and $x=1\%$, respectively. The nature of the pinning is determined for each type of doping, and we evaluate the size of the domains of coherence of the charge-density waves. [S0163-1829(99)03520-1]

I. INTRODUCTION

The influence of defects on the Peierls instability of quasi one-dimensional (1D) materials such as NbSe$_3$ has long been studied because of their drastic effects on the electronic properties.[1] In 1D systems, the Peierls instability leads to the formation at low temperature of a periodic modulation of the conduction electron density called the charge-density wave (CDW). This CDW is accompanied by a periodic lattice distortion (PLD) $\mathbf{u}(\mathbf{r})$ of the same period, in a quadrature with the CDW, which can be written

$$\mathbf{u}(\mathbf{r})=\mathbf{u}_0\cos(\mathbf{q}\cdot\mathbf{r}+\Phi),$$

where $\mathbf{q}$ is a wave vector, whose component along the one-dimensional direction is $2k_F$ (k_F is the Fermi wave vector). The order parameter of the phase transition is defined as $\mathbf{U}=\mathbf{u}_0e^{i\Phi}$. When $2k_F$ is incommensurate with respect to the reciprocal-lattice parameter, Φ has no preferred value. Consequently, in an ideal crystal, the application of an arbitrarily small electric field would cause the CDW to slide through the crystal. In real crystals, however, impurities and other defects actually prevent such a sliding, unless the applied electric field is in excess of a threshold value. A microscopic theory of the pinning [the so-called (FLR) theory[2]] was initially set up by considering the competition between the energy gain due to the adjustment of the CDW phase $(\mathbf{q}\cdot\mathbf{r})+\Phi(\mathbf{r})$ on each impurity, and the cost of elastic energy to be paid for the resulting phase deformation. Depending on the relative importance of these two energies, two extreme cases can be considered: strong and weak pinning. In the strong (individual) pinning case, where the impurity potential dominates, the phase is fixed to a given value on each impurity position. In the weak (collective) pinning case, $\Phi(\mathbf{r})$ adjusts to a constant value inside a so-called FLR domain containing several impurities. In both cases the CDW long-range order (LRO) is lost. The consequence of these two limits of pinning on the structure of the CDW's is that in the low-temperature phase the CDW order is broken in domains of coherence, each containing one impurity in the strong pinning case and more than one impurity in the weak pinning case. Although this distinction is oversimplified since both small- and large-scale variations of the phase of the CDW are theoretically expected,[3] it is helpful to discriminate in a simple way the nature of the pinning in doped materials. However, providing experimental evidence of the nature of the pinning has always been a difficult task, as illustrated by the controversial results on threshold fields data in Ta- and Ti-doped NbSe$_3$.[4]

The structure of CDW's can be probed by x-ray-diffraction experiments. In the low-temperature phase, when the CDW LRO is established, the PLD gives rise to resolution limited satellite reflections at $\pm\mathbf{q}$ around each main Bragg reflection, whose intensities are proportional to the square of the modulus of the order parameter $\mathbf{U}$. Above the critical temperature T_c, where only fluctuations of the CDW order parameter are present, the satellite reflections broaden. Their intensity is proportional to the Fourier transform of the correlation function $\langle\mathbf{u}(0)\mathbf{u}(\mathbf{r})\rangle$, and they have a Lorentzian line shape with a half-width at half-maximum (HWHM) inversely proportional to the CDW correlation lengths.[5] At low temperature, assuming that the amplitude fluctuations of the CDW are negligible, the satellite intensity is proportional to the Fourier transform of the spatial-averaged phase-phase correlation function $\langle e^{i(\Phi(\mathbf{r})-\Phi(0))}\rangle$.[6] In that case, the shape and width of the satellite reflections give information on the structure of the CDW phase. In pure NbSe$_3$, high-resolution x-ray scattering experiments performed at low temperature have shown that the width of the CDW satellite reflections are either resolution limited[7] or limited by the transverse size of the crystal itself along directions orthogonal to $2k_F$.[6] Both results indicate a true 3D long-range order of the CDW at low temperature, at the scale of the crystal.

The influence of a random distribution of impurities on the CDW order can be studied by x-ray scattering experiments in different ways. First, as the defects destroy the CDW long-range order, the satellite reflections broaden. The HWHM's of these satellite reflections are inversely proportional to the coherence length, or domain size of the CDW. Second, the shape of the satellite reflections, properly deconvoluted from the experimental resolution, gives the spatial decay of the phase-phase correlation function. High-resolution x-ray-diffraction studies in Ta-doped NbSe$_3$,[6] and V- and W-doped blue bronzes[8] have always yielded an ex-

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ponential decay of the phase-phase correlation function: $\langle e^{i(\Phi(\mathbf{r})-\Phi(0))}\rangle \sim e^{-|\mathbf{r}|/l}$. Such a decay corresponds to an intrinsic Lorentzian-squared line shape of the satellite reflection. Finally, a more recently discovered x-ray-diffraction effect can provide a deeper insight into the nature of the pinning. In the strong pinning case, the spatial coherence between the defect positions and the phase of the PLD gives rise to an asymmetry of the intensities of the $\pm\mathbf{q}$ satellite reflections.[9] Strong asymmetries (the so-called ''white-line'' effect) have already been observed and analyzed in alloys of organic conductors.[9,10] In this paper, we report on a study of $NbSe_3$ heavily doped ($\simeq 1\%$) with two different types of impurities, Ti and Ta.

II. EXPERIMENT

$NbSe_3$ is a linear-chain material which crystallizes in the $P(2_1/m)$ space group,[11] with the lattice parameters $a = 10$ Å, $b = 3.48$ Å, $c = 15.62$ Å, and $\beta = 109.47°$. As in the other transition metal trichalcogenides MX_3, irregular $NbSe_6$ prisms stack in the **b** direction. Three types of chains, labeled I, II, and III, can be distinguished depending on the Se-Se bond length of the basis of the prism. The unit cell consists of three pairs of chains of each type. $NbSe_3$ undergoes two independent Peierls transitions at the critical temperatures $T_{c1} = 145$ K and $T_{c2} = 59$ K, which stabilize a CDW, respectively, on type-III chains at the reduced wave vector $\mathbf{q}_1 = (0,q_1,0)$, and on type-I chains at the reduced wave vector $\mathbf{q}_2 = (0.5,q_2,0.5)$, with $q_1 = 0.241$ and $q_2 = 0.259$ at $T = 15$ K.[12]

In $NbSe_3$, the niobium atoms can be substituted for either by elements of the same column, like tantalum, or by other transition elements, like titanium. Tantalum and niobium are isoelectronic and have a similar size, whereas titanium has one electron less and is smaller than niobium. An x-ray-diffraction study of slightly Ta-doped crystal has already been carried out, confirming the weak pinning nature of the CDW pinning.[6] Here we investigate the effect of Ta and Ti impurities in heavily doped crystals. The influence of each type of doping on the three-dimensional $\mathbf{q}_1$-CDW sublattice has been obtained by measuring the size of the domains of coherence of the CDW's. We have also investigated the possibility of having a $\pm\mathbf{q}$ asymmetry of the diffuse scattering intensities.

The samples were prepared in Cornell University by using a vapor-transport growth procedure. The impurity concentration n was characterized by the residual resistance ratio $r = R(300\ \mathrm{K})/R(4.2\ \mathrm{K}) \propto 1/n$. We have studied two samples: a Ta-doped crystal with $r = 1.4$ ($n_{Ta} \simeq 2\%$) and a Ti-doped one with $r = 2$ ($n_{Ti} \simeq 1\%$). X-ray Weissenberg experiments were carried out on both samples to check that the crystal structure was unchanged upon doping.

X-ray experiments were performed with a low-temperature (300–10 K) diffractometer with a lifting-detector geometry. We used Cu K_α radiation from a rotating anode generator, obtained after a (002) reflection on a doubly bent graphite monochromator. The resolution function was measured on the $(\bar{1},2,0)$ Bragg reflection at 15 K, near the satellite reflection under investigation. A fit by a Gaussian line shape gave us the HWHM's along the $\mathbf{b}^*$, **a**, and $\mathbf{c}^*$ directions. With this procedure, the resolutions along the $\mathbf{b}^*$, **a**, and $\mathbf{c}^*$ directions were found to be equal to 0.024, 0.023, and 0.035 Å^{-1}, respectively, for the Ti-doped sample and 0.022, 0.010, and 0.024 Å^{-1}, respectively, for the Ta-doped sample. Scans through $(\bar{1},2\pm q_1,0)$ were performed along the three directions $\mathbf{b}^*$, **a**, and $\mathbf{c}^*$ as a function of temperature. All the scans were fitted by a one-dimensional convolution of a parametrized function with the Gaussian resolution function in order to extract the intrinsic width of the satellite reflections.

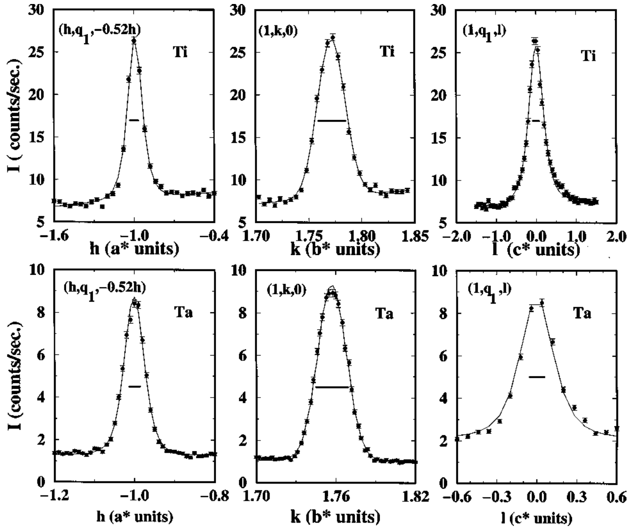

FIG. 1. Scans along the **a**, $\mathbf{b}^*$, and $\mathbf{c}^*$ directions of the $\mathbf{q}_1$ satellite peak in 1%-Ti- and 2%-Ta-doped $NbSe_3$ at 20 K. Horizontal bars represent the full-width at half-maximum of the resolution. The lines are the result of the convolution of the Lorentzian-squared profile with the resolution.

III. RESULTS

Typical scans through the $(\bar{1},2-q_1,0)$ position along the $\mathbf{b}^*$, **a**, and $\mathbf{c}^*$ directions at T=20 K for both type of doping are shown in Fig. 1. These scans clearly show that the diffuse scattering peaks are larger than the experimental resolution. This indicates the loss of the LRO of the CDW, even at low temperature. The position of the diffuse peak along $\mathbf{b}^*$ was found to be at the reduced wave vector $q_1 = 0.227(2)$ in the Ti-doped sample, and at the pure $NbSe_3$ value $q_1 = 0.241(2)$ in the Ta-doped sample. We extracted the intrinsic domain size of the CDW ordering by fitting the experimental scans by a convolution of the Gaussian experimental resolution and a Lorentzian-squared profile (see Fig. 1). Compared to other line shapes (Gaussian, Lorentzian), this Lorentzian-squared line shape improved the fit only slightly, but was chosen for consistency with high-resolution synchrotron radiation experiments on similar doped materials.[6,8]

The temperature dependence of the maximum of the $(\bar{1},2-q_1,0)$ peak $I(\mathbf{q}_1)$ for both types of doping is plotted in Fig. 2 together with that of the pure compound. For pure $NbSe_3$, the intensity of the satellite peak continuously decreases toward the critical temperature T_{c1}. In doped compounds, the intensity is much weaker, and the intensity vs temperature differs. The curve of the Ta-doped sample exhibits an inflection point around the temperature $T^* = 110$ K before saturating at low temperatures, whereas the

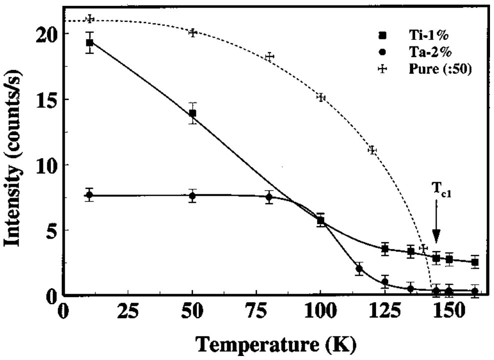

FIG. 2. Temperature dependence of the $\mathbf{q}_1$ satellite peak intensity in 1%-Ti and 2%-Ta doped $NbSe_3$ (solid lines) and in pure $NbSe_3$ (dotted line). Crosses represent the experimental peak intensities of pure $NbSe_3$, with an attenuation factor of 50. The intensities are not normalized.

curve for Ti-doped sample continuously increases when temperature decreases.

Figure 3 displays the thermal variations of the HWHM's obtained after deconvolution for the doped compounds. The HWHM's do not go to zero at T_{c1}, as observed in the pure compound. Values of the HWHM's are smaller in the Ta-doped sample than in the Ti-doped sample. As usual, we define the dimensional crossover between 3D and 2D domains when the HWHM along $\mathbf{c}^*$ exceeds $c^*/2\pi = 0.068$ Å^{-1}. At low temperature, whereas the CDW domain of coherence is essentially 2D for the Ti-1% doping, it becomes 3D for the Ta-doped crystal. Also, the HWHM's in the three directions decrease monotonically with temperature in Ti-1%, while they saturate below T^* in Ta-2%. It is noteworthy that such a saturation of the HWHM's was also observed in Ta-0.25% below ~120 K. The CDW coherence lengths l_{b^*}, l_a and l_{c^*} at 20 K (with a Lorentzian-squared profile, $l = 0.6436/\mathrm{HWHM}$) are equal respectively to 27, 14, and 7 Å for the Ti-doped sample, and 170, 40, and 15 Å in the Ta-doped one. The anisotropy ratio shows that the domain of coherence is more isotropic for the Ti-doped sample where $l_{b^*}:l_a:l_{c^*} = 4:2:1$, than for the Ta-doped sample where $l_{b^*}:l_a:l_{c^*} = 11:3:1$.

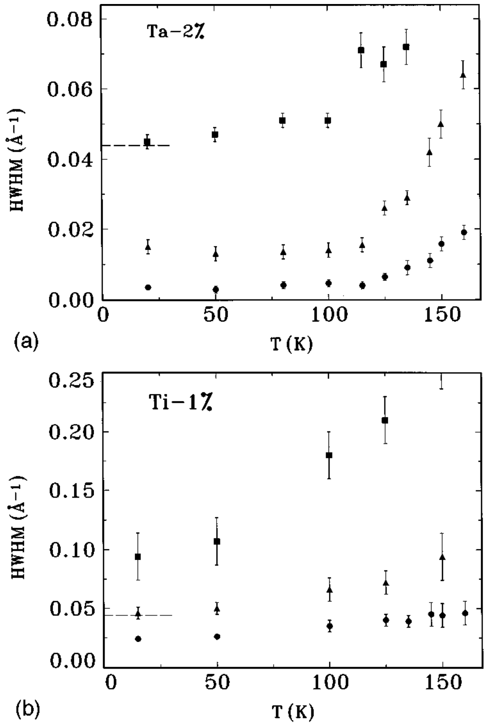

FIG. 3. Temperature dependence of the intrinsic HWHM's of the $\mathbf{q}_1$ peak in the 2%-Ta (top) and 1%-Ti (bottom) doped $NbSe_3$. Circles, triangles, and squares correspond to the HWHM's along the $\mathbf{b}^*$, $\mathbf{a}$, and $\mathbf{c}^*$ directions, respectively. The horizontal dashed lines at $0.6436c^*/2\pi$ correspond to the dimensionality crossover explained in the text.

We investigated the possibility of the occurrence of an interference effect in the doped compounds by measuring the intensity ratio of the $-\mathbf{q}_1/+\mathbf{q}_1$ diffuse peaks on each side of the $(\bar{1},2,0)$ Bragg reflection in each doped sample. This ratio in the pure compound was measured equal to 1.37(2), and no significant deviation from this value was found in the doped compounds. Let us recall that such an asymmetry of diffuse scattering was detected by photograph techniques in a Ti-5% doped sample.[13]

IV. DISCUSSION

Let us first discuss the possible positions of tantalum and titanium in the $NbSe_3$ structure. The MX_3 compounds crystallize in three main structural arrangements, with one, two, or three different types of chains in the unit cell.[14] The structure of $TaSe_3$ contains two chains, which, according to the Se-Se pair bond length, are similar to type-I and -II chains of $NbSe_3$. On the other hand, although $TiSe_3$ does not exist, TiS_3 and $ZrSe_3$ contains only one type of chain similar to the type-III chains of $NbSe_3$. This could suggest that the Ta impurity preferentially substitutes Nb on type-I and -II chains, and than the Ti substitutes the Nb on type-III chains. However, these hypotheses have never been checked by structure refinements.

Consistent with our choice of a Lorentzian-squared fitting function, we will assume a random distribution of CDW-correlated domains sizes.[15] Then, from the value of coherence lengths at 20 K, we can evaluate the number of pinning centers (PC's) present in the CDW domain of coherence. For Ti-1%, this domain is $l_{b^*} \times l_a \times l_{c^*} \sim 2600$ Å^3. As the volume of the unit cell is 542 Å^3, this domain of coherence corresponds to five unit cells. Assuming a *random* distribution of impurities over the six possible niobium sites in the unit cell, there is only 0.06 Ti per unit cell for 1% doping, i.e., 0.3 Ti per domain of coherence. If one assumes that only the Ti located on chain III acts as a pinning center, there is only 0.1 PC per domain of coherence. If, as stated above, the Ti impurities preferentially substitute the Nb atoms on chain III, one obtains 0.9 PC per domain of coherence. These values show that the Ti-1% crystal is in the strong pinning limit. Nevertheless, the small values obtained here suggest the existence of CDW domains which do not contain PC's. Now let us consider the case of the Ta substitution. The domain of coherence of the Ta-2% doped crystal corresponds to 188 unit cells. This is to be compared with the results obtained by DiCarlo *et al.*[6] on a Ta-0.25% doped crystal ($r = 10$), where a value of 45 000 PC's per domain of coherence was found. If there is random substitution of tantalum over the three types of chains, there are 0.12 Ta per unit cell (24 Ta per domain of coherence) and thus eight PC's if only the tantalum atoms substituted on chain III are considered as PC's. These large numbers rather indicate a weak pinning situation. In addition, the strength of the pinning could be quite weak if, as indicated previously, the tantalum atoms ''prefer'' to substitute Nb atoms on type-I and -II chains.

So far, the anisotropy ratio $l_{b*}:l_a:l_{c*}$ measured on doped crystal are 4:2:1, 11:3:1, and 12:4:1 in Ti-1%, Ta-2%, and Ta-0.25%,[6] respectively. This is to be compared with the anisotropy of the correlation lengths above the $\mathbf{q}_1$ Peierls phase transition 27:8:1.[7] It appears clearly that doping decreases the anisotropy of the domains of coherence. This is especially striking in the Ti doping case, where the transverse CDW coherence spreads approximately over three type-III chains in the **a** direction, and one chain in the **c** direction. This anisotropy is consistent with a strong pinning scenario, in which the domain of coherence is expected to be limited by the average distance between impurities. In that case, the anisotropy of the domains is only reminiscent of the correlation length anisotropy of the pure compound. Concerning the Ta-doped case, the coherence takes place over several chains and is then more 3D. Nevertheless, the large anisotropy observed in the pure compound correlation length is not observed.

The difference between the nature of the two types of doping and their respective influence on the CDW texture is also shown by the temperature dependence of the peak intensity $I(\mathbf{q}_1)$ and that of the HWHM's. The concomitant observation of a saturation of the HWHM's and of an inflection point in the temperature behavior of $I(\mathbf{q}_1)$ indicates that the CDW texture is frozen in below T^* in Ta-2%. This allows us to define a pseudo-phase-transition at T^*, below which there is an increase of the ''order parameter.'' Such a pseudotransition does not exist for the Ti-doped sample. In that case the CDW domain size still increases at low temperature. This behavior is reminiscent of a coarsening phenomena, where small domains collapse in larger ones, observed for example in binary alloys.[16] Interestingly enough, the same effects have been observed in the V-2.8% and W-2% doped blue bronzes,[8] where the impurity substitute the Mo atoms involved in the CDW.

The variation of the wave-vector position in the Ti-doped compound is due to the filling of the electronic band structure with one electron less with the element Ti^{4+} with respect to Nb^{5+}. According to Ref. 17, two electrons partially fill four bands out of six, which gives an average $\langle 2k_F\rangle = 0.25$, experimentally observed. Assuming that all the conduction bands are equally affected by the substitution, doping by x Ti^{4+} will let $(2-6x)$ electrons into the conducting bands, which leads to $\langle 2k_F\rangle = (0.25-0.75x)$. For $x=1\%$, the relative variation $\Delta 2k_F$ of the Fermi wave vector is

$$\frac{\Delta 2k_F}{\langle 2k_F\rangle} = -3x = -3\%.$$

Our experiments gives, $\Delta q_1/q_{1pure} = 0.014/0.241 = -5.8\% \pm 0.8\%$. This could indicate that the Ti atoms preferentially empty the two conduction bands originating from the type-III chains.

Finally, let us discuss the absence of $\pm 2k_F$ intensity asymmetries in the Ti-1% compound despite the strong pinning. This contrasts with the V-2.8% doped blue bronze,[8] where clear $\pm 2k_F$ asymmetries have been observed. As the intensity asymmetry is proportional to the impurity concentration,[9] the simplest explanation is that the doping level is too small in our crystal to give rise to the effect. This is all the more true if only part of the impurities act as pinning centers. Second, this effect is maximum when the domain of coherence is 1D, as has been established in organic materials,[9] which is not the case in the Ti-1% crystal. At the least, our estimation of the number of impurities per domain of coherence suggests that some domains do not contain impurities and thus do not contribute to the asymmetry effect. However, $\pm 2k_F$ intensity asymmetries have been detected in a previous photographic investigation of a Ti-5% compound.[13] With respect to the Ti-1% compound, the intensity asymmetry can be caused both by the increase by a factor 5 of the impurity concentration and by the formation of 1D CDW coherence domains. The decrease of the $-2k_F$ intensity with respect to the $+2k_F$ one indicates that the Nb-atom neighbors of the Ti atoms are displaced away from the impurity. Let us remark that this finding is opposite to elastic effects, where it is expected that the Nb atoms move toward the Ti of smaller size. The effect, previously observed in V-doped blue bronzes,[8] is attributed to a pinning mechanism of electronic origin. We thus suggest that the titanium Ti^{4+}, which appears as a negative charge in the background of Nb^{5+}, is screened by adjusting the positively charged part of the CDW on the impurity site. The presence of an excess of positive charge around the impurity thus repels the Nb ions away from the Ti.

In summary, we have studied the effect of a heavy doping of isoelectronic (Ta) and nonisoelectronic (Ti) impurities on the structure of the CDW in NbSe$_3$. The structure of the CDW's at low temperature are consistent with a strong pinning in the Ti-1% case, and a weak pinning in the Ta-2% case. A pseudo-phase-transition is still visible in the Ta-doped crystal, while a continuous coarsening of the CDW domains of coherence is observed in the Ti-doped crystal.

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