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Brief Reports

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Determination of the structural distortions corresponding to the $\mathbf{q}^1$- and $\mathbf{q}^2$-type modulations in niobium triselenide $NbSe_3$

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Synchrotron-radiation single-crystal x-ray diffraction is used to study the modulations corresponding to both the $\mathbf{q}^1$-and $\mathbf{q}^2$-type charge-density waves (CDW's) in $NbSe_3$. The $\mathbf{q}^1$-type modulation is shown to involve displacements of the atoms of column III. The $\mathbf{q}^2$-type modulation is analogous, but resides on column I. An important feature is that it is found that both CDW's involve displacements of a Se atom of column II. This structure explains previous experiments, but appears to be at variance with the more recently obtained scanning-tunneling-microscopy images. The implications for the dimensionality of the $\mathbf{q}^1$ transition are discussed.

The unusual electrical properties of niobium triselenide ($NbSe_3$) are related to the presence at low temperatures of two independent charge-density-waves (CDW's).[1] Notwithstanding the extensive number of studies that have been reported, no quantitative information about the structural distortions due to the CDW's is available.[2] In the present paper we report the determination of the atomic displacements due to both charge density waves, from synchrotron intensity data collected at 20 K.

The basic structure of $NbSe_3$ has monoclinic, $P2_1/m$, symmetry. It consists of columns of face-sharing triangular prisms of selenium atoms parallel to the unique monoclinic **b** axis, with a niobium atom at the center of each prism. Adjacent columns are shifted over $\mathbf{b}/2$, thus leading to an eightfold coordination of Nb by Se (Fig. 1). There are three crystallographically independent niobium atoms, defining three types of columns, labeled I, II, and III, respectively.

The first CDW develops below $T_{c1} \simeq 145$ K, and is characterized by a modulation wave vector $\mathbf{q}^1 = (0, 0.241, 0)$. The second CDW exists below $T_{c2} = 59$ K, and has a modulation wave vector $\mathbf{q}^2 = (\frac{1}{2}, 0.260, \frac{1}{2})$. (The components refer to the basis-structure unit cell.[2,3]) It was proposed that the $\mathbf{q}^1$-type CDW occurs on a quasi-one-dimensional d band on the niobium type-III atoms, whereas the second CDW resides on the type-I columns.[4] Subsequent band-structure calculations support this hypothesis.[5-7] NMR experiments, probing the niobium atoms, showed that only two of the three columns are involved in the transitions.[8] The $\mathbf{q}^1$-type

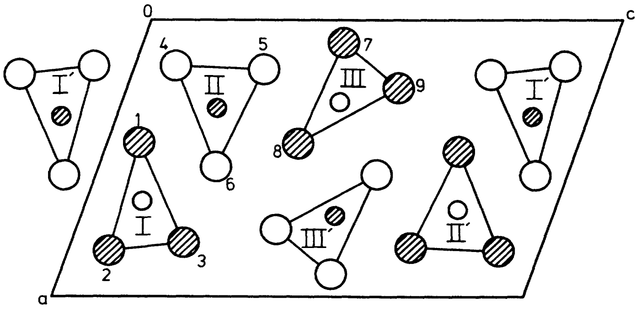

FIG. 1. Projection along **b** of a part of the structure of one unit cell thickness. Small and large circles denote Nb and Se atoms, respectively. Open circles correspond to atoms at $z = \frac{1}{4}$; hatched circles represent atoms at $z = \frac{3}{4}$. Arabic numbers correspond to the Se atoms in Table I. Primed numbers indicate symmetry equivalent columns.

modulation could be assigned to the Nb(III) atoms, the columns involved in the $\mathbf{q}^2$-type transition could not be assigned unambiguously.[8,9] Diffraction work also showed that the $\mathbf{q}^1$-type modulation principally involves a displacement of Nb(III).[10]

Recent scanning-tunneling-microscope (STM) experiments reopened the discussion about the nature of the CDW's.[11–14] Dai *et al.*[14] concluded from their measurements that strong CDW's are present on all three columns, the $\mathbf{q}^1$-type CDW residing on the type-III column, and the $\mathbf{q}^2$ CDW corresponding to both columns I and II. The STM results appear at variance with results from other experiments, in particular those done with NMR.[8]

In a comment[15,16] we pointed out the difficulties that exist in relating STM results, which depend on surface electronic states near the Fermi level,[17] to the atomic and electronic structure. The present study shows that the primary structural distortion accompanying both CDW's is a displacement of Nb(III) for the $\mathbf{q}^1$-type modulation and a displacement of Nb(I) for the $\mathbf{q}^2$-type modulation. However, major displacements are also found on all Se atoms coordinating Nb(III) (for the $\mathbf{q}^1$ modulation) and coordinating Nb(I) (for the $\mathbf{q}^2$-type modulation), including the Se atoms on column II. This type of distortion involves most of the Se atoms on column II, but not Nb(II).

A single crystal of $\mathrm{NbSe_3}$ of dimensions $15\times3000\times25\mu m^3$, along $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$, respectively, was used for measuring single-crystal x-ray-diffraction intensities on the SUNY Beam line X3 at the National Synchrotron Light Source at Brookhaven National Laboratory. After data reduction a set of 972 unique reflections was obtained (377 main reflections, 433 $\mathbf{q}^1$-type satellites, and 162 $\mathbf{q}^2$-type satellites) with $I>2\sigma(\mathrm{I})$. The superspace-group symmetry[18] was determined from the extinction conditions. To facilitate the analysis, a two-fold supercell was adopted, with $\mathbf{A}=\mathbf{a}+\mathbf{c}$, $\mathbf{B}=\mathbf{b}$, and $\mathbf{C}=-\mathbf{a}+\mathbf{c}$. With respect to this supercell and its reciprocal, the second modulation wave vector becomes $\mathbf{q}_i^2=(0,0.260,0)$, whereas $\mathbf{q}^1$ remains unchanged. The symmetry operators are

$$(2_1\ s\ 1)=(2_y\ 1\ 1|0,\tfrac{1}{2},0,\tfrac{1}{2},0);$$

$$(m_y\ \bar{1}\ \bar{1})=(m_y\ \bar{1}\ \bar{1}\ |0,\tfrac{1}{2},0,\tfrac{1}{2},0);$$

$$(i\ \bar{1}\ \bar{1})=(i\ \bar{1}\ \bar{1}\ |0,0,0,0,0)$$

and the centering translation $(E\ 1\ 1\ |\tfrac{1}{2},0,\tfrac{1}{2},0,\tfrac{1}{2})$. The symbol to the right of the equal sign denotes the rotational part juxtaposed to the five translational components. The second and third symbols in each operator designate whether R_{44} and R_{55} are 1 or -1. The symbol to the left of the equal sign denotes the rotational part of the symmetry operator together with the intrinsic translational part i.e., s meaning a screw component of $\frac{1}{2}$ along the fourth or fifth superspace coordinate. A tentative symbol for the superspace group is $P{:}P2_1/m(0,\beta,0)(1/2,\beta',1/2)s\bar{1};1\bar{1}$.

As found in earlier studies the basic structure is essentially independent of the temperature.[3] At $T=20$ K we find the lattice parameters $a=9.974(1)$ Å, $b=3.476(2)$Å, $c=15.592(2)$ Å, and $\beta=109.4(1)°$. The basic structure parameters obtained from the refinement are given in Table I. They differ only marginally from the coordinates reported for 100 K.[3] Because all atoms are in a mirror plane, symmetry restrictions apply to the basic structure coordinates as well as to the modulation functions. For the symmetry operators given above, we find for the modulation function of each atom:

$$\begin{aligned}\mathbf{u}(\bar{x}_4,\bar{x}_5)= {} & [B_x^1\sin(2\pi\bar{x}_4)+A_x^2\cos(2\pi\bar{x}_5)]\,\mathbf{A}\\ & +[A_y^1\cos(2\pi\bar{x}_4)+B_y^2\sin(2\pi\bar{x}_5)]\mathbf{B}\\ & +[B_z^1\sin(2\pi\bar{x}_4)+A_z^2\cos(2\pi\bar{x}_5)]\mathbf{C}. \qquad (1)\end{aligned}$$

As only first-order satellites were observed for each modulation type, higher harmonics were not included. The fourth and fifth superspace coordinates are defined as $\bar{x}_4=\mathbf{q}^1\cdot\mathbf{r}^0$ and $\bar{x}_5=\mathbf{q}_i^2\cdot\mathbf{r}^0$, with $\mathbf{r}^0$ the basic structure position. Refinements of the basic structure parameters and 36 amplitudes for each modulation type were performed against 972 reflection intensities, using the program JANA.[19] The final agreement factor is $R_F=\sum||F_{\mathrm{obs}}|$

TABLE I. Structural parameters for $\mathrm{NbSe_3}$. Basic structure coordinates are relative to the supercell $\{\mathbf{A},\mathbf{B},\mathbf{C}\}$. Modulation parameters are defined according to Eq. (1), but are given in angstrom along the supercell axes. Standard deviations in the last digit are in parentheses.

Atom	x	y	z	B_x^1	A_y^1	B_z^1	A_x^2	B_y^2	A_z^2
Nb(1)	0.3858(1)	0.25	−0.2674(1)	0.002(1)	0.003(1)	−0.004(1)	0.006(2)	0.025(2)	−0.001(2)
Nb(2)	0.2615(1)	0.75	−0.0552(1)	0.002(1)	0.008(1)	−0.007(1)	0.006(2)	0.005(2)	−0.006(2)
Nb(3)	0.3780(1)	0.25	0.0837(1)	0.012(2)	0.053(1)	−0.007(1)	0.001(2)	0.004(2)	−0.001(2)
Se(1)	0.2539(2)	0.75	−0.1868(1)	0.002(2)	0.001(2)	−0.004(2)	0.013(3)	0.003(2)	−0.008(3)
Se(2)	0.4601(2)	0.75	−0.3733(1)	0.001(2)	−0.001(2)	−0.004(2)	−0.006(3)	0.005(3)	0.013(3)
Se(3)	0.5212(2)	0.75	−0.2826(1)	0.004(2)	−0.002(2)	−0.004(2)	−0.010(3)	0.012(3)	0.012(3)
Se(4)	0.1260(2)	0.25	−0.0393(1)	−0.001(2)	−0.001(2)	−0.002(2)	0.004(3)	0.001(3)	0.001(3)
Se(5)	0.2273(2)	0.25	0.0491(1)	0.011(2)	0.017(2)	−0.006(2)	0.004(3)	0.000(2)	0.005(3)
Se(6)	0.3881(2)	0.25	−0.1397(1)	0.006(2)	−0.000(2)	−0.007(2)	0.005(3)	0.012(3)	0.001(3)
Se(7)	0.2534(2)	0.75	0.171691)	−0.007(2)	0.021(2)	0.031(2)	0.001(3)	0.001(3)	−0.005(3)
Se(8)	0.4246(2)	0.75	−0.0195(1)	0.021(2)	−0.007(2)	−0.027(2)	0.001(3)	0.003(3)	0.001(3)
Se(9)	0.4099(2)	0.75	0.1658(1)	−0.002(2)	0.014(2)	0.021(2)	−0.001(3)	0.001(3)	−0.002(3)

$-|F_{\mathrm{calc}}||/\sum|F_{\mathrm{obs}}|=0.077$. Partial R factors, defined for a subset of the reflections, are $R_F=0.073$ for main reflections only, $R_F=0.11$ for the $\mathbf{q}^1$-type satellites, and $R_F=0.18$ for the $\mathbf{q}^2$-type satellites. The higher values for the satellite R factors reflect that, on the average, these reflections have a lower $I/\sigma(\mathrm{I})$ ratio than the main reflections. The $\mathbf{q}^2$-type reflections are weaker than the $\mathbf{q}^1$-type satellites. The final modulation amplitudes are given in Table I.

From Table I it follows that the principal components of the modulation waves are a displacement of Nb(III) for the $\mathbf{q}^1$-type distortion and a displacement of Nb(I) for the $\mathbf{q}^2$-type modulation, in accordance with the model of Wilson.[4] It is noted that the modulation is very small: the largest amplitude is 0.05 Å and is found on one atom [Nb(III)] only. Displacements of secondary importance are found on all Se atoms coordinating the modulated Nb atoms. This includes the Se atoms on column II, i.e., Se(5) for the $\mathbf{q}^1$ modulation and Se(6) for the $\mathbf{q}^2$ modulation. It is of importance that the amplitudes for the $\mathbf{q}^1$ modulation on chain I and for the $\mathbf{q}^2$ modulation on chain III are much smaller than 0.01 Å. This means that both modulations do not extend beyond their neighboring columns, which in each case is the type-II column.

If only monoclinic centrosymmetric symmetry is considered, there are two possibilities for the $\mathbf{q}^1$ modulation, one leading to a superspace group with $(2_1\ 1\ 1)$ elements and one leading to a superspace group with $(2_1\ s\ 1)$ elements. These two possibilities could be distinguished on the basis of the extinction conditions and the superspace group belonging to the structure. Apparently the latter type of symmetry elements are found in the structure. For the second modulation type there is but a single superspace group, which contains both elements $(2_1\ s\ 1)$ and $(2_1\ s\ s)$. Then there are two possibilities for the position of the type-I columns in the unit cell. The strongly bonded pair of columns (I, I′) can be related across a $(2_1\ s\ 1)$ or across a $(2_1\ s\ s)$ element. The structure refinement shows the latter to be correct. It thus follows from our structure refinement that the phasing of the $\mathbf{q}^1$ CDW on the pairs (III, III′) is identical to the phasing of the $\mathbf{q}^2$ CDW on the pairs (I, I′), again showing the similar nature of both CDW's.

The atomic displacements can be understood entirely in terms of two independent CDW's, residing on the Nb(III) and Nb(I) chains, respectively, combined with the effect of internal strain. In order to minimize the variation in bond length, the selenium atoms follow the displacements of the niobium atoms to which they are bonded. The same applies to the strongly bonded Se_2^{2-} ions [Se(7) with Se(9) and Se(2) with Se(3)], for which it is found that both atoms are displaced in phase. To obtain the coordinates and displacements of chain III′, adjacent to III (Fig. 1), the symmetry operator $(2_y\ 1\ 1\ |1,\frac{1}{2},0,\frac{1}{2},0)$ has to be applied to the parameters in Table I. With Δz equal to $\frac{1}{2}$, this means that the modulation of Nb(III′) is out of phase by $\frac{5}{8}$ from Nb(III). For the given $\mathbf{q}^1$ vector this must be the phase difference giving the least possible strain (as compared to $\frac{1}{8}$).

It is a general understanding that a CDW, as occurs in the valence band, is correlated with the accompanying structural distortion. Recently, Moudden *et al.*[10] have found that structural displacements belonging to the CDW fluctuations above T_{c1} are mainly in the $(\mathbf{a},\mathbf{b})$ plane, indicating a two-dimensional system in this direction. With the results obtained here, a better understanding of the dimensionality of NbSe_3 can be obtained. Analysis of bond distances shows NbSe_3 to be a two-dimensional system in the $(\mathbf{b},\mathbf{c})$ plane. However, the interaction between neighboring columns III along $\mathbf{c}$ involves eight bonds, going from one Nb(III) to the next. Analysis of the modulation amplitudes for $\mathbf{q}^1$ shows that this type of modulation has negligible amplitudes on the atoms of column I, i.e., halfway such a path. The amplitudes should be even smaller close to the transition temperature.[20] This means that the interaction between the modulations on neighboring columns III is very small along $\mathbf{c}$, thus explaining the small correlation length parallel to $\mathbf{c}^*$ above T_{c1}. The interaction along $\mathbf{a}$ involves a path of only two Nb—Se bonds and a single nonbonded interaction. The latter is between Se atoms which have a relatively large modulation amplitude, and thus can be expected to interact relatively strongly. This provides an explanation for the two-dimensional character of the CDW in terms of elastic interactions between the atoms. It also shows that it is not necessary to assume that the electron band has a 2D rather than a 1D character. It is likely that other properties (e.g., most of the phonons, cleavage) are two dimensional in the $(\mathbf{a},\mathbf{b})$ plane rather than in the $(\mathbf{b},\mathbf{c})$ plane.

In summary, we have presented complete structural information concerning the atomic displacements belonging to both types of modulations in NbSe_3. It was shown that $\mathbf{q}^1$ primarily involves a displacement of Nb(III), but that relatively large amplitudes are found on all neighboring Se atoms, including the one on column II. The same picture is obtained for $\mathbf{q}^2$, albeit with smaller amplitudes, and now for a displacement primarily on Nb(I). The results fully support the interpretation of the formation of a CDW on the Nb chains, where the displacements of the other atoms follow from elastic intra- and inter-chain interactions.

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[1] P. Monceau, in *Electronic Properties of Inorganic Quasi-one-Dimensional Compounds, Physics and Chemistry of Materials with Low Dimensional Structures,* Ser. B., edited by P. Monceau (Reidel, Dordrecht, 1985).

[2] A. Meerschaut and J. Rouxel, in *Crystal Chemistry and Properties of Materials with Quasi-One-Dimensional Structures, Physics and Chemistry of Materials with Low Dimensional Structures,* Ser. B, edited by J. Rouxel (Reidel, Dordrecht, 1986), p. 205–279.

[3] J. L. Hodeau, M. Marezio, C. Roucau, R. Ayroles, A. Meerschaut, J. Rouxel, and P. Monceau, J. Phys. C **11**, 4117 (1978).

[4] J. A. Wilson, Phys. Rev. B **19**, 6456 (1979).

[5] D. W. Bullet, J. Phys. C **12**, 277 (1979).

[6] R. Hoffmann, S. Shaik, J. C. Scott, M.-H. Whangbo, and M. J. Foshee, J. Solid State Chem. **34**, 263 (1980).

[7] M.-H. Whangbo and P. Gressier, Inorg. Chem. **23**, 1305 (1984).

[8] F. Devreux, J. Phys. **43**, 1489 (1982).

[9] J. H. Ross, Jr., A. Wang, and C. P. Slichter, Phys. Rev. Lett. **56**, 663 (1986).

[10] A. H. Moudden, J. D. Axe, P. Monceau, and F. Levy, Phys. Rev. Lett. **65**, 223 (1990).

[11] R. V. Coleman, B. Giambattista, A. Johnson, W. W. McNairy, G. Slough, P. K. Hansma, and B. Drake, J. Vac. Sci. Technol. A **6**, 338 (1988).

[12] C. G. Slough, B. Giambattista, A. Johnson, W. W. McNairy, and R. V. Coleman, Phys. Rev. B **39**, 5496 (1989).

[13] G. Gammie, J. S. Hubacek, S. L. Skala, R. T. Brockenbrough, J. R. Tucker, and J. W. Lyding, Phys. Rev. B **40**, 9529 (1989).

[14] Z. Dai, C. G. Slough, and R. V. Coleman, Phys. Rev. Lett. **66**, 1318 (1991).

[15] S. van Smaalen, J. L. de Boer, P. Coppens, and H. Graafsma, Phys. Rev. Lett. **67**, 1471 (1991).

[16] Z. Dai, C. G. Slough, and R. V. Coleman, Phys. Rev. Lett. **67**, 1472 (1991).

[17] J. Tersoff, Phys. Rev. Lett. **57**, 440 (1986).

[18] A. Janner, T. Janssen, and P. M. De Wolff, Acta Crystallogr. A **39**, 671 (1983).

[19] V. Petricek, P. Coppens, and P. J. Becker, Acta Crystallogr. A **41**, 478 (1985).

[20] R. M. Fleming, D. E. Moncton, and D. B. McWhan, Phys. Rev. B **18**, 5560 (1978).