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Anomalous-scattering contrast study of the mixed-valence charge-density-wave conductor NbSe$_3$

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Abstract. The *valence-contrast* diffraction method is used at the Nb *K* edge in the analysis of the mixed-valence solid NbSe$_3$. The NbSe$_3$ structure consists of three parallel chains of prismatically coordinated Nb atoms and undergoes two low-temperature Peierls-type phase transitions that lead to modulated structures. Previous analysis of synchrotron-radiation single-crystal data has shown that the transition that occurs on cooling at 145 K (leading to the $\mathbf{q}_1$-type modulation) involves displacements of Nb$_{\rm III}$ atoms as well as of some of the coordinated Se atoms, while the second transition (the $\mathbf{q}_2$-type modulation), at 59 K, involves displacements of Nb$_{\rm I}$ atoms and an Se atom of column II [van Smaalen, de Boer, Meetsma, Graafsma, Sheu, Darovskikh, Coppens & Levy (1992). *Phys. Rev. B*, **45**, 3103–3106]. The present room-temperature study, performed at seven different wavelengths in the vicinity of the Nb absorption edge, shows the Nb$_{\rm II}$-atom edge to be shifted to higher energies by about 5 eV relative to those of the other Nb atoms. This indicates a smaller population of the Nb$_{\rm II}$-atom conduction band, in agreement with band-structure calculations but not with conclusions derived from nuclear magnetic resonance measurements.

Introduction. The unusual non-ohmic electrical properties of niobium triselenide (NbSe$_3$) are related to the occurrence at low temperature of two independent charge-density waves (CDW's) (Meerschaut & Rouxel, 1985).

The basic structure of NbSe$_3$ has monoclinic $P2_1/m$ symmetry. It consists of columns of face-sharing triangular prisms of Se atoms, parallel to the monoclinic *b* axis, with an Nb atom at the center of each prism (Fig. 1; Hodeau, Marezio, Roucau, Ayroles, Meerschaut, Rouxel & Monceau, 1978). There are three crystallographically independent Nb atoms, defining three types of columns, labelled I, II and III, respectively.

The first CDW develops below $T_{c1} \sim 145$ 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 $\mathbf{q}_2 = (1/2, 0.260, 1/2)$ (van Smaalen, de Boer, Meetsma, Graafsma, Sheu, Darovskikh, Coppens & Levy, 1992; Hodeau *et al.*, 1978). Our recent low-temperature diffraction results (van Smaalen *et al.*, 1992) confirm earlier conclusions, based on nuclear magnetic resonance (NMR) studies of ^{93}Nb (Devreux, 1982), that only two of the three chains distort at low temperature, the Nb$_{\rm II}$ atoms being essentially unaffected. As the distortion opens a gap at the Fermi level of each of the chains, this implies a difference in the filling of their conduction bands. The band of the non-distorting chain may be either completely filled or essentially empty. Wilson (1979) proposed an ionic model, according to which 28 of the 30 (5*s*, 4*d*) valence electrons of the six Nb atoms in the unit cell are distributed over four (Se–Se)$^{2-}$ and ten Se^{2-} ions. This model is in agreement with observed Se–Se bond dis-

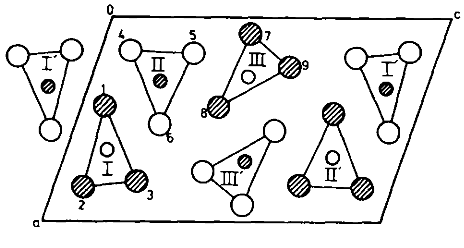

Fig. 1. Projection of the structure along **b**. Small and large circles denote Nb and Se atoms, respectively. Open and hatched circles correspond to atoms at $z = 1/4$ and $z = 3/4$, respectively. Roman numbers represent column types as well as the Nb atoms. Primed numbers indicate symmetry-equivalent columns.

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tances. The remaining two electrons are distributed over the two $\mathrm{Nb_{I}}$ and two $\mathrm{Nb_{III}}$ ions, leading to 1/4-filled bands of chains I and III, in agreement with the observed **q** vectors, and predicting a nonpopulated band on chain II.

Subsequent band-structure calculations qualitatively support this hypothesis (Bullet, 1979; Hoffmann, Shaik, Scott, Whangbo & Foshee, 1980; Whangbo & Gressier, 1984). Population analysis of the band-structure calculations of Whangbo & Gressier (1984), for example, shows two low-lying empty bands to have strong $\mathrm{Nb_{II}}$-atom characteristics, consistent with Wilson's (1979) model of a more positive $\mathrm{Nb_{II}}$ ion. On the other hand, the ^{93}Nb NMR experiments were interpreted in terms of a model in which four out of six d_{z^2} electrons (one from each of the six Nb atoms in the cell) completely fill the two $\mathrm{Nb_{II}}$-atom bands, while the remaining two are distributed over the four $\mathrm{Nb_{I}}$- and $\mathrm{Nb_{III}}$-atom bands, thus predicting a more negative $\mathrm{Nb_{II}}$ atom (Devreux, 1982). A more recent point-charge field-gradient calculation by Ross, Wang & Slichter (1990) shows, however, that the NMR results are also compatible with net atomic charges according to the Wilson (1979) model.

Experimental. All experiments were done at station *A*2 of the SUNY X3 beam line at the National Synchrotron Light Source (NSLS).

NEXAFS (*near-edge X-ray absorption fine structure*). The dependence of the niobium scattering factor on the valence state was confirmed by f' curves for niobium metal and NbO_2 (Fig. 2), derived by Kramers–Kronig transformation of the absorption spectra measured on powders. As expected, the Nb atom in the oxide has a higher 1*s* binding energy, the difference being about 10 eV, in qualitative agreement with shifts observed for vanadium oxides (Wong, Lytle, Mesmer & Maylotte, 1984) and other transition-metal atoms (Manthiram, Sarode, Madhusudan, Gopalakrishnan & Rao, 1980).

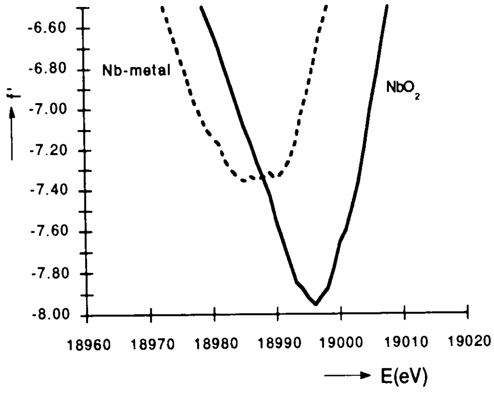

Fig. 2. f' values for niobium metal and NbO_2, derived from powder-absorption measurements.

Table 1. *f' values from refinement of hkl reflections* (*data set* I)

Energy	$\mathrm{Nb_{I}}$	$\mathrm{Nb_{II}}$	$\mathrm{Nb_{III}}$	$R(F)/R_w(F)$ %
18931	-5.8(11)	-5.9(11)	-5.4(12)	4.05/4.18
18961	-6.4(10)	-8.4(10)	-7.0(11)	4.08/4.22
18971	-8.3(11)	-9.9(10)	-8.3(11)	3.90/4.22
18981	-4.9(11)	-8.6(10)	-6.3(12)	4.14/4.17
18991	-5.7(14)	-7.8(14)	-5.1(15)	4.97/5.25
19001	-4.4(12)	-7.5(12)	-5.7(12)	4.94/4.73

Diffraction. A single crystal of $NbSe_3$, of dimensions 0.025 × 0.002 × 5 mm, elongated along the *b* axis, was obtained from R. E. Thorne of Cornell University and used for measuring sets of 33 reflections at six wavelengths in the vicinity of the Nb *K*-absorption edge. To eliminate as far as possible the effects of synchrotron instabilities, every second reflection measured was a standard reflection, the intensity of which was used in the scaling of the data. The absorption coefficients for niobium were obtained from the EXAFS curve and put on an absolute scale by a fit to the theoretical values of Cromer & Liberman (1970). After data reduction, reflection intensities were analyzed by the least-squares method, using published values of the positional and thermal parameters (Hodeau *et al.*, 1978). The scale factor and the f' values of the three Nb atoms were the variables in the refinement. The f'' values were kept constant at values derived from the absorption measurements. They have little effect on the refinement as the structure is centrosymmetric. To investigate possibly significant anisotropy of f', a second refinement was performed with only the 25 reflections with scattering vectors within 30° of the *h*0*l* plane, for which the polarization vector of the incident beam is close to parallel to the chain axis. To test reproducibility, the *h*0*l* data were recollected in a subsequent experimental run (one of the six wavelengths in this second experiment was selected differently) and refined independently (data set II). Results of the refinements are given in Tables 1–3. The agreement between the two *h*0*l* data sets is well within the standard deviations (Tables 2 and 3).

Analysis. The results of the full data-set refinement indicate that the $\mathrm{Nb_{II}}$-atom f' curve is shifted to a higher energy compared to the $\mathrm{Nb_{I}}$- and $\mathrm{Nb_{III}}$-atom curves. This is most clearly seen by comparing the f' values at two points at either side of the minimum f' value; although the minimum value for all three atoms is at 18971 eV, the f' values at 18961 eV are lower than those at 18981 eV for $\mathrm{Nb_{I}}$ and $\mathrm{Nb_{III}}$ atoms but less negative for $\mathrm{Nb_{II}}$ atoms. To obtain a more quantitative estimate of the shift, the expression

$$f' = (g_k/x^2)\ln|x^2 - 1| + \Delta,$$

Table 2. *f' values from refinement of h0l reflections* (*data set* I)

Energy	Nb_I	Nb_{II}	Nb_{III}	$R(F)/R_w(F)$ %
18931	-4.6(9)	-6.0(8)	-6.6(8)	2.76/2.93
18961	-5.6(10)	-8.2(8)	-8.1(9)	3.39/3.50
18971	-7.0(8)	-9.8(7)	-9.5(7)	2.96/2.79
18981	-3.1(9)	-9.2(8)	-7.1(9)	3.57/2.87
18991	-4.0(9)	-7.5(8)	-6.9(9)	3.49/3.12
19001	-3.8(13)	-7.2(13)	-6.4(12)	4.67/4.65

Table 3. *f' values from refinement of h0l reflections* (*data set* II)

Energy	Nb_I	Nb_{II}	Nb_{III}	$R(F)/R_w(F)$ %
18951	-3.4(9)	-8.0(8)	-7.7(9)	3.12/2.65
18961	-4.7(6)	-7.7(5)	-8.0(6)	2.07/1.83
18971	-5.9(6)	-8.9(5)	-9.6(6)	2.20/1.89
18981	-3.3(8)	-8.0(7)	-7.8(8)	2.61/2.39
18991	-3.0(8)	-7.0(7)	-7.1(8)	2.71/2.41
19001	-3.4(9)	-6.9(9)	-7.0(9)	3.06/2.80

based on an empirical equation given by James (1982), with $x = E/E_0$, has been fitted to all six points. The adjustable parameters are the oscillator strength, g_k, E_0 and Δ, a parameter added to the James equation to allow for a vertical shift of the curves. A similar fit was done on the average of the two *h*0*l* data sets. Although the equation reproduces the data points only approximately (Fig. 3), as might be expected because it neglects any fine structure, as well as instrumental broadening and the effect of finite energy-level widths, the resulting values of the f' minima are in agreement with the qualitative conclusions reached earlier.

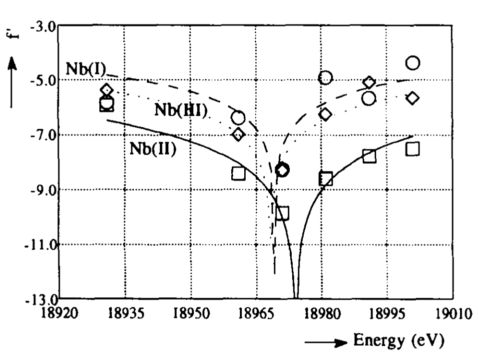

Fig. 3. Fit to f' values derived from all *hkl* data of set I. Circles correspond to Nb_I atoms, squares to Nb_{II} atoms, diamonds to Nb_{III} atoms.

Table 4. *Relative binding energies, E_0* (eV) *of* Nb *atoms determined from curve fitting*

Atoms	*h*0*l* Reflections (Data Set I & II)	*hkl* Reflections (Data sets I)
Nb_I	18969.9(60)	18969.2(54)
Nb_{II}	18973.9(20)	18974.0(18)
Nb_{III}	18968.4(24)	18968.3(24)
$E_0\{Nb_{II}\}-E_0\{Nb_{I,III}\}$	4.7	5.2

The *h*0*l* data, for which the X-ray polarization vector is approximately parallel to the niobium chain axis, give similar results (Fig. 4, Table 4). The Nb_{II}-atom minimum is again at the highest energy. The f' values of the Nb_I atoms are significantly less negative, which suggests that the transitions from the *K* edge for Nb_I atoms are generally less allowed when the polarization vector is parallel to the *b* axis.

The absolute energy scale of the niobium results deserves comment. Although the f' minima in Figs. 2 and 3 are below those of niobium metal and NbO_2, we believe the shift to be an artefact of the experimental procedures and not a true energy shift. Thus, only the relative values for the f' minima should be considered.

Concluding remarks. The anomalous-scattering experiments show the Nb_{II} $1s$ electrons to have the larger binding energies, which implies a more positively charged ion. The observed shift of about 5 eV corresponds to two valence units, if the absorption results for niobium metal and NbO_2 are taken as a measure. However, since a population analysis would certainly show that the Nb atom in NbO_2 does not lose four valence electrons upon oxidation, the difference between the Nb_{II} and Nb_I/Nb_{III} populations is certainly less than two electrons. The recent NMR results of Shi & Ross (1992) show that the Nb_{II} chains have a non-vanishing density of states at the Fermi level, so the conduction band cannot be fully depleted. Nevertheless, our results are in qualitative agreement with the Wilson

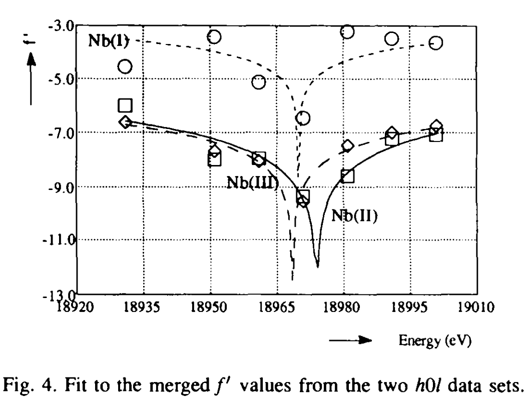

Fig. 4. Fit to the merged f' values from the two *h*0*l* data sets.

(1979) model, which predicts a difference of II in formal valency (*i.e.* IV for $\mathrm{Nb_I}$ and $\mathrm{Nb_{III}}$; VI for $\mathrm{Nb_{II}}$) and a 0.5 e difference in net charge, and the Whangbo & Gressier (1984) theoretical results, according to which $\mathrm{Nb_{II}}$ is more positive than the other Nb ions. The present study demonstrates the value of the valence-contrast method in providing information on the electronic structure from wavelength-dependent diffraction measurements.

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