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Preparation and Structure of $(NbSe_4)_{3.33}I$. $[I_3Nb_{10}Se_{40}]$

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The structural determination of a novel linear chain compound $(NbSe_4)_{3.33}I$ is reported. The structure was solved by means of Patterson and Fourier syntheses and refined to $R = 0.030$, $R_W = 0.040$, for 566 independent reflexions [$I \geq 3\sigma$ (I)]. The structure is built up of infinite $[NbSe_4]$ chains along the c axis (tetragonal symmetry). Iodine atoms are located within the channels between these chains. The iodine atoms do not show the same distribution within all the channels as is the case for related compounds such as $(NbSe_4)_3I$, $(TaSe_4)_2I$. This new compound undergoes a phase transition at 285 K associated with a change density wave (CDW) origin.

Introduction

Chemical investigations in the field of chalcogen-rich niobium and tantalum chalcogenides have led to the characterization of new trichalcogenides among which $NbSe_3$ (*1*) and monoclinic TaS_3 (*2*) are undoubtedly the most interesting species. These low-dimensional compounds are subject to phase transitions such as Peierls transitions or charge density wave (CDW) instabilities. $NbSe_3$ and monoclinic TaS_3 show evidence for the first time of a collective transport mode associated with the motion of a CDW as demonstrated by the nonlinear conductivity observed above a threshold electric field (*3*).

In the course of these studies another series of compounds were prepared. They are the halogen-tetrachalcogenides $(MX_4)_nY$ (where M = Nb, Ta; X = S, Se; Y = Cl, Br, I; $n \geq 2$). Illustrated at first by $(NbSe_4)_3I$ these compounds have been the subject of structural determinations and physical measurements (*4*). We are concerned with a very promising class of pseudo one-dimensional materials which are candidates for CDW transport phenomena. In the present work we describe a new member of the series with a complex formulation $(NbSe_4)_{3.33}I$ (n = 10/3 instead of n = 2, 3 . . . as usual). The structure has been determined and is discussed in relation with the transport measurements.

Experimental

$(NbSe_4)_{3.33}I$ crystals have been picked up from preparations made in an attempt to obtain $MgNb_3Se_{10}$ as a new compound with the $FeNb_3Se_{10}$ structural type (*5*). Mixtures of the elements in stoichiometric proportions were heated under vacuum in sealed evacuated silica tubes at 700°C for 15 days with iodine as transport agent. Chemical analyses by means of an electron micro-

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TABLE I

$(NbSe_4)_{3.33}I$ INDEXED POWDER DIFFRACTION PATTERN

I/I_0[a]	d_{mes}	d_{calc}	h	k	l	I/I_0[a]	d_{mes}	d_{calc}	h	k	l
95	6.696	6.692	1	1	0	60	2.3665	2.3661	4	0	0
5	6.095	6.099	1	0	4	80	2.3100	2.3093	2	2	10
5	5.325	5.318	0	0	6	20	2.2897	2.2895	4	1	1
60	4.736	4.732	2	0	0	30	2.2459	2.2438	4	1	3
10	4.235	4.233	2	1	0	20	2.2307	2.2308	3	3	0
20	4.163	4.164	1	1	6	70	2.1821	2.1830	3	1	10
60	4.093	4.091	2	1	2	90	2.1171	2.1163	4	2	0
50	3.938	3.933	2	1	3	5	2.0515	2.0502	4	1	7
40	3.742	3.739	2	1	4	70	2.0088	2.0087	4	2	5
50	3.678	3.676	1	0	8	2	1.9904	1.9895	4	1	8
10	3.539	3.535	2	0	6	50	1.8790	1.8797	4	3	2
10	3.3115	3.3118	2	1	6	70	1.8569	1.8561	5	1	0
90	3.1884	3.1910	0	0	10	5	1.7549	1.7575	5	2	0
30	3.1004	3.1017	2	1	7	60	1.7471	1.7469	5	2	2
40	2.9946	2.9929	3	1	0	50	1.7340	1.7339	3	1	15
20	2.8796	2.8803	1	1	10	40	1.7144	1.7163	5	2	4
20	2.8323	2.8322	2	2	6	40	1.7106	1.7101	5	0	8
100	2.7096	2.7097	3	1	5	40	1.6726	1.6731	4	4	0
90	2.6451	2.6457	2	0	10	20	1.6231	1.6231	5	3	0
5	2.6063	2.6083	3	1	6	80	1.5953	1.5955	0	0	20
60	2.5913	2.5901	3	2	2	10	1.5776	1.5774	6	0	0
5	2.5495	2.5480	2	1	10	20	1.5514	1.5524	5	3	6
5	2.4923	2.4934	3	2	4	10	1.5409	1.5395	6	1	3
20	2.4740	2.4744	3	0	8						

[a] Estimated intensities.

probe analyzer (microsonde OUEST-CNEXO) of these crystals proved their correct formulation to be $(NbSe_4)_{3.33}I$ (% experimental Nb = 20.8, Se = 71.0, I = 8.1; % theoretical: Nb = 20.8, Se = 70.7, I = 8.5). This formulation was confirmed by the structural determination.

Single crystal X-ray analysis shows $(NbSe_4)_{3.33}I$ to be tetragonal, space group $P4/mcc$. The unit cell parameters $a = 9.464$ (1) Å, $c = 31.910$ (8) Å were refined from Guinier powder data (Guinier-Nonius FR 552), λ $CuK\alpha_1 = 1.54051$ Å, Si: internal standard) (Table I).

The crystal selected for data collection was mounted on a Nonius CAD 4 diffractometer. Information about the intensity data collection are given in Table II; 3944 independent reflexions were corrected for Lorentz and polarization factors. An absorption correction was applied to the data based on the indexed crystal faces {100},

TABLE II

PARAMETERS OF THE X-RAY DATA COLLECTION

Dimensions: 0.022 × 0.03 × 0.36 mm, the longest along the c axis
Absorption factor $\mu(\lambda\ MoK\alpha) = 287\ cm^{-1}$
Radiation $MoK\alpha$: graphite monochromator
Scan mode: ω
θ Range: $2° < \theta < 37°$
$I > 3\sigma(I)$: 566 independent reflexions
$R = \Sigma|KF_0 - |F_c||/\Sigma kF_0 = 0.030$
$R_\omega = [\Sigma\omega(kF_0 - |F_c|)^2/\Sigma\omega k^2F_0^2]^{1/2} = 0.040$
Weighting scheme 1 nonpoisson contribution fudge factor $p = 0.05$, cutoff = 3

TABLE III

Positional and Thermal Parameters and Their Estimated Standard Deviations

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{eq} (Å^2)
$\mathrm{Nb_1}$	0	$\frac{1}{2}$	$\frac{1}{4}$	0.0029 (3)	0.0034 (3)	0.00083 (4)	0	0	0	1.88 (7)
$\mathrm{Nb_2}$	0	$\frac{1}{2}$	0.4506 (1)	0.0030 (2)	0.0031 (2)	0.00097 (3)	0.0000 (4)	0	0	2.06 (5)
$\mathrm{Nb_3}$	0	$\frac{1}{2}$	0.3494 (1)	0.0030 (2)	0.0028 (2)	0.00106 (3)	0.0003 (4)	0	0	2.13 (5)
$\mathrm{I_1}$	0	0	0.4205 (1)	0.0045 (2)	0.0045 (2)	0.00268 (6)	0	0	0	4.72 (7)
$\mathrm{I_2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{4}$	0.0045 (3)	0.0045 (3)	0.0044 (1)	0	0	0	7.1 (2)
$\mathrm{Se_1}$	0.3159 (2)	0.1272 (2)	0.40282 (7)	0.0033 (2)	0.0034 (2)	0.00099 (3)	0.0008 (3)	0.0001 (3)	−0.0000 (1)	2.15 (4)
$\mathrm{Se_2}$	0.8084 (2)	0.3788 (2)	0.29646 (7)	0.0029 (2)	0.0040 (2)	0.00104 (2)	−0.0010 (3)	0.0002 (1)	−0.0000 (1)	2.25 (4)
$\mathrm{Se_3}$	0.7208 (2)	0.0364 (2)	0.30257 (6)	0.0033 (2)	0.0046 (2)	0.00104 (2)	−0.0015 (4)	−0.0001 (2)	−0.0001 (1)	2.35 (4)
$\mathrm{Se_4}$	0.7831 (2)	0.5500 (2)	0.39673 (6)	0.0033 (2)	0.0035 (2)	0.00108 (2)	0.0008 (3)	0.0000 (1)	−0.0000 (1)	2.28 (4)
$\mathrm{Se_5}$	0.8925 (3)	0.7001 (3)	$\frac{1}{2}$	0.0048 (3)	0.0039 (3)	0.00103 (4)	0.0020 (6)	0	0	2.44 (6)
$\mathrm{Se_6}$	0.4798 (3)	0.2233 (3)	$\frac{1}{2}$	0.0054 (3)	0.0036 (3)	0.00095 (3)	0.0003 (6)	0	0	2.37 (6)

Note. The form of the anisotropic thermal parameter is $B_{eq} = \frac{4}{3} \sum_{ij} (\mathbf{a}_i \cdot \mathbf{a}_j)\beta_{ij}$; $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

$\{010\}$, $\{\bar{1}00\}$, $\{0\bar{1}0\}$, $\{001\}$, $\{00\bar{1}\}$ using a $8 \times 8 \times 8$ grid. The crystal shape is approximated as a parallelepiped which dimensions were $0.022 \times 0.03 \times 0.36$ mm, the longest one corresponding to the c axis.

The structure was solved from Patterson and Fourier maps and refined by full matrix least squares, minimizing the quantity $\Sigma\omega(|F_0| - |F_c|)^2$. The structure was further refined with anisotropic temperature factors assigned to all atoms. Refinement converged with $R = 0.030$, $R_W = 0.040$. The goodness of fit, $[\Sigma\omega(\Delta F)^2/(NO - NV)]^{1/2}$ for the last cycle was 1.028 with $NO = 566$ and $NV = 68$, NO and NV being respectively the number of observations and variables. The final difference Fourier map was featureless (1.1 (3) e.Å^{-3}). Scattering factors for neutral atoms were taken from the International Tables (*6*) and corrected for anomalous dispersion. An isotropic extinction correction was included in the final stage of refinement; its value was 2.56×10^{-8}. All calculations were performed with SDP Enraf-Nonius programs written by Frenz (*7*).

The positional and thermal parameters are summarized in Table III. A list of observed and calculated structure factors can be obtained from the authors upon request.

Description and Discussion of the Structure

$(\mathrm{NbSe_4})_{3.33}\mathrm{I}$ exhibits a structure which reveals a marked one-dimensional character. Figure 1 shows the projection of the structure on the XYO plane. $[\mathrm{NbSe_4}]$ columns are aligned along the c axis and iodine atoms are located within the channels which develop between these one-dimensional $[\mathrm{NbSe_4}]$ chains. There is an obvious structural analogy with $(\mathrm{NbSe_4})_3\mathrm{I}$ although the structure of $(\mathrm{NbSe_4})_{3.33}\mathrm{I}$ is more complex in detail. Indeed, if the a parameter is unaltered, the c parameter of $(\mathrm{NbSe_4})_{3.33}\mathrm{I}$ is 10/6 times that of $(\mathrm{NbSe_4})_3\mathrm{I}$: Figure 2 shows the projection of the structure on the $x0z$ plane. Niobium atoms aligned along the linear chain are not equally distributed. The bond alternation is represented by the sequence:

$$\begin{array}{cccccccc}
\text{———} & \mathrm{Nb}_2 & \overset{3.232\ \text{Å}}{\text{———}} & \mathrm{Nb}_3 & \overset{3.171\ \text{Å}}{\text{———}} & \mathrm{Nb}_1 & \overset{3.171\ \text{Å}}{\text{———}} & \\
\downarrow & & & & & \downarrow & & \\
0 & & \to Z \text{ values} & & & 1/4 & & \\
 & & & \mathrm{Nb}_3 & \overset{3.232\ \text{Å}}{\text{———}} & \mathrm{Nb}_2 & \overset{3.150\ \text{Å}}{\text{———}} & \mathrm{Nb}_2 \\
 & & & & & \downarrow & & \\
 & & & & & 1/2 & &
\end{array}$$

The coordination of niobium is a rectangular antiprism which is composed of four

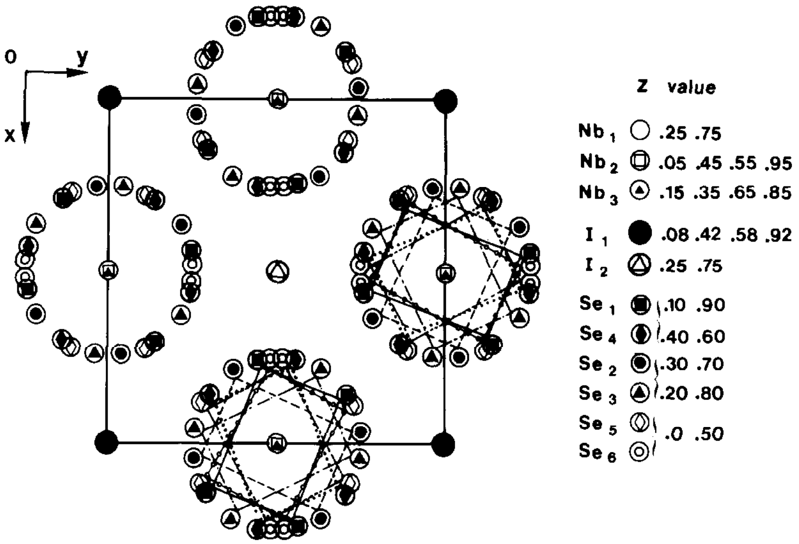

FIG. 1. Projection of the $(NbSe_4)_{10/3}I$ structure on to the $xy0$ plane.

(Se_2) pairs (see Fig. 3). The dimensions of each rectangle are about 3.5 and 2.35 Å (see Table IV), the latter value corresponding to the typical $(Se_2)^{2-}$ pairing. The antiprisms are stacked on top of each other in a screwlike arrangement along the c axis.

The iodine atoms do not show the same distribution within all the channels as is observed in the cases of $(NbSe_4)_3I$ and $(TaSe_4)_2I$. In this case we can distinguish between two types of channels; one along the $00z$ axis which is filled by four iodine atoms, the other along the $\frac{1}{2}\frac{1}{2}z$ axis, which is occupied by only two iodine atoms. In the first case, iodine atoms are closely bonded to four selenium atoms (I − 4Se = 3.272 Å) while in the second case, iodine atoms are rather weakly bonded to eight

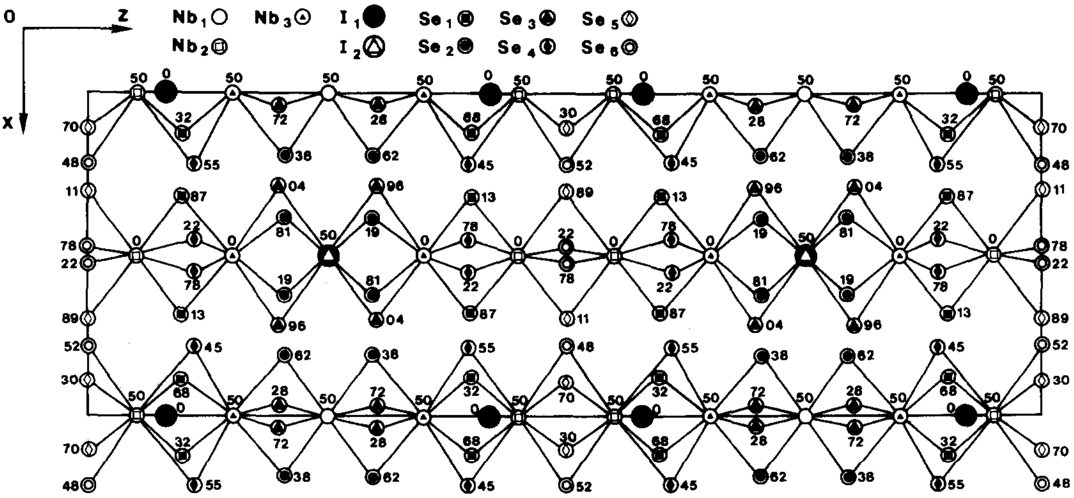

FIG. 2. Projection of the $(NbSe_4)_{10/3}I$ structure on to the $x0z$ plane.

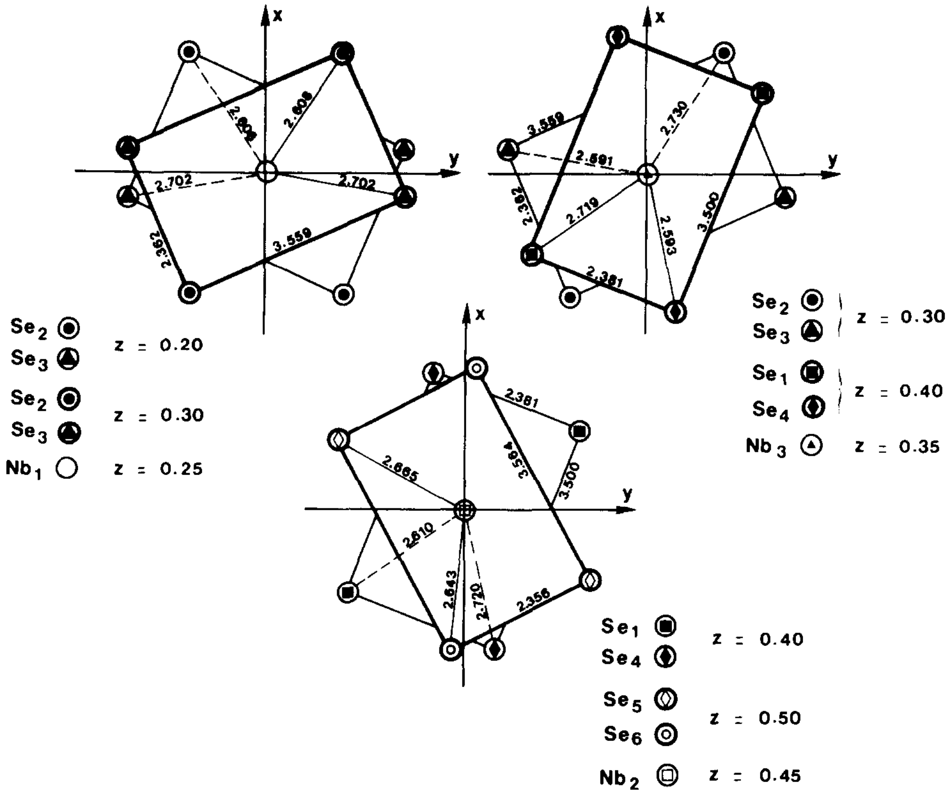

FIG. 3. Rectangular antiprismatic $[NbSe_8]$ polyhedron.

selenium atoms (I − 8Se = 3.469 Å) in a square antiprismatic arrangement (see Figs. 4a and b). This determines three kinds of selenium planes according to the degree of bonding with iodine:

The first is characterized by Se atoms in a strong interaction with iodine (I_1 − 4Se = 3.272 (2) Å).

The second is associated with Se atoms in a weaker interaction with iodine, such as I_2 − 8Se = 3.469 (3) Å.

The third plane corresponds to unaffected Se atoms. This plane is rigorously perpendicular to the niobium chain and is consequently attached to the shortest Nb—Nb length along the chain (Fig. 5).

TABLE IV

INTERATOMIC DISTANCES (Å) IN $[NbSe_8]$

$Nb_1 - 4\,Se_2$	2.608 (3)	$Nb_3 - 2\,Se_2$	2.730 (4)	$Nb_2 - 2\,Se_5$	2.665 (4)
$Nb_1 - 4\,Se_3$	2.702 (2)	$Nb_3 - 2\,Se_3$	2.591 (3)	$Nb_2 - 2\,Se_6$	2.643 (3)
		$Nb_3 - 2\,Se_1$	2.719 (3)	$Nb_2 - 2\,Se_1$	2.610 (3)
		$Nb_3 - 2\,Se_4$	2.593 (3)	$Nb_2 - 2\,Se_4$	2.720 (3)
$Se_2 - Se_3$	2.362 (4) 3.559 (4)	$Se_1 - Se_4$	2.381 (3) 3.500 (3)	$Se_5 - Se_6$	2.356 (6) 3.564 (6)
$Nb_1 - Nb_3$	3.171 (3)	$Nb_2 - Nb_3$	3.232 (5)	$Nb_2 - Nb_2$	3.150 (7)

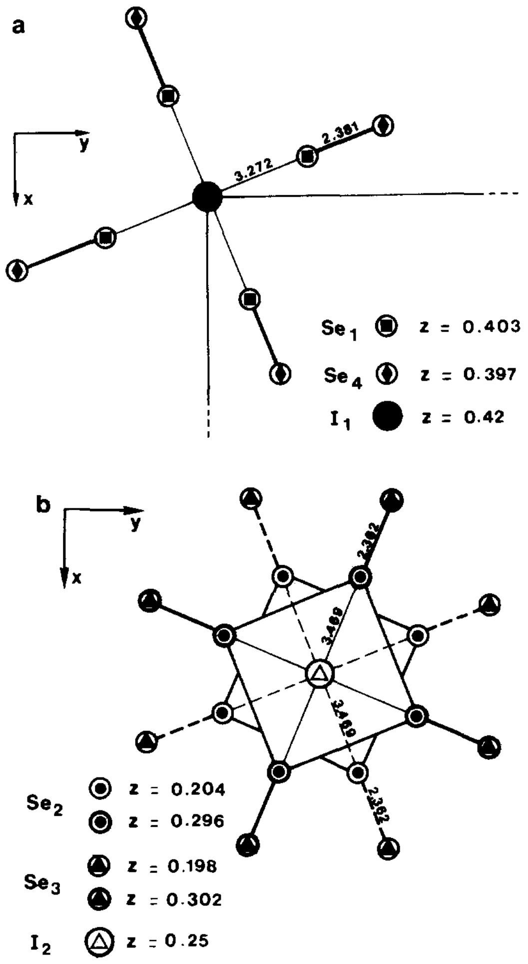

FIG. 4. (a) Iodine atom coordinated to 4 selenium atoms; iodine atom located along the 00z axis. (b) Iodine atom coordinated to 8 selenium atoms; iodine atom located along the $\frac{1}{2}\frac{1}{2}z$ axis.

The strength of the iodine–selenium interaction is indirectly manifested in the Se—Se distances in the (Se$_2$) pairs. Indeed, one observes in the structure three short Se—Se distances corresponding to three types of Se$_2$ pairs, (Se (1) − Se (4) = 2.381 Å, Se (2) − Se (3) = 2.362 Å and Se (5) − Se (6) = 2.356 Å). As the greatest of these values corresponds to the shortest I—Se distance (3.272 Å), we can assume that a charge transfer takes place from the Se—Se pair toward iodine, decreasing the subsequent I—Se bond length and correlatively increasing the Se—Se bond length.

XPS measurements on (NbSe$_4$)$_3$I were consistent with this assumption (*8*). In that case, the Se 3*d* spectrum was better fitted with two Se signals in a 2 : 1 ratio, the ratio of the selenium planes, unaffected and affected by iodine, respectively. XPS measurement on (NbSe$_4$)$_{3.33}$I, will be performed very soon to test these remarks.

Physical Measurements

Resistivity measurements were performed by a four-probes method using a low frequency bridge (33 Hz). Four contacts were made with silver paint. The room temperature resistivity along the needle axis is about $1.5 \times 10^{-2}\ \Omega \cdot$ cm, which is about 2 orders of magnitude less than that of (NbSe$_4$)$_3$I (*4*). A simple explanation can be given through the intermetallic bonds sequence. As noted above, the Nb—Nb sequence in (NbSe$_4$)$_{3.33}$I contains three different lengths (3.232, 3.171, and 3.150 Å); (NbSe$_4$)$_3$I contains two long and one short Nb—Nb distances (3.251 and 3.060 Å). The greater difference in lengths in (NbSe$_4$)$_3$I produces a weaker delocalization of electrons and thus a greater resistivity.

The resistivity variation with temperature (Fig. 6) agrees with a thermal activated mechanism (E = 0.13 eV). A transition is observed at 285 K (see the derivative curve). This type of curve strongly recalls that of many one-dimensional systems and particularly TaS$_3$ (orthorhombic and monoclinic forms). In such one-dimensional systems the corresponding transition is associated with structural instabilities of the Peierls type or induced by a charge density wave. Some preliminary investigations on (NbSe$_4$)$_{3.33}$I crystals show clearly nonlinear effects related to the depinning and subsequent sliding motion of the CDW. This will be the subject of a further investigation of

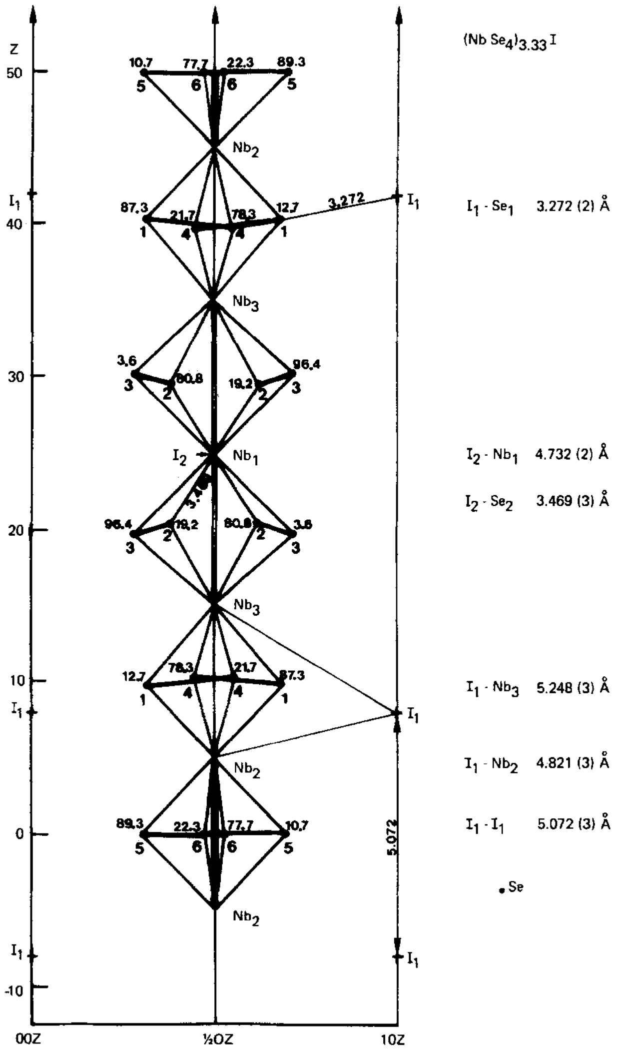

FIG. 5. $[NbSe_4]$ chain running in a parallel direction to the c axis.

the material in cooperation with Monceau (9).

Conclusion

$(NbSe_4)_{3.33}I$ is a new member of the $(MX_4)_nY$ family. It has a more complex structure than other members of this class of compounds. These compounds complete the wide family of chalcogenide halides of group VB elements with other members having different formulations and structures as reported by Schnering *et al.* (10) and Rijnsdorp (11).

$(NbSe_4)_{3.33}I$ undergoes an electrical transition at 285 K. Current–voltage measurements (9) indicate nonlinear effects implying the very likely occurrence of a CDW transition which will be examined by the usual systematic studies (electronic diffraction, pressure and Hall effect . . .).

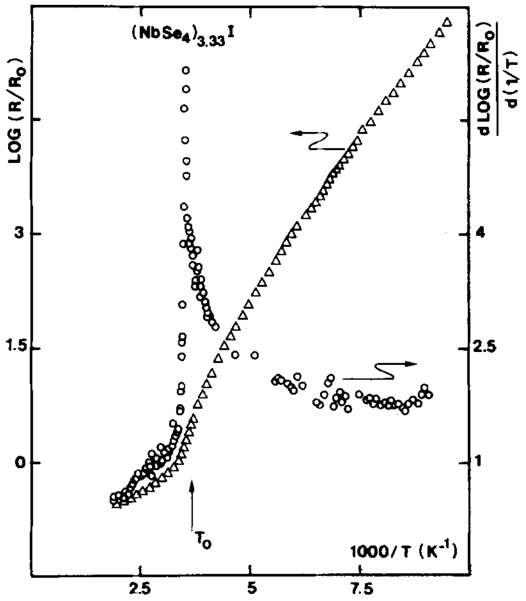

FIG. 6. Log (R/R_0) versus $10^3/T$ for $(NbSe_4)_{10/3}I$.

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