

## The Crystal Structure of NbSe<sub>2</sub> at 15°K

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At 40°K the 2H polytype of NbSe<sub>2</sub> undergoes a transition which is accompanied by anomalies in the electrical resistivity and Hall effect. However, our magnetic susceptibility measurements do not show a pronounced anomaly at the transition. The crystal structure of 2H-NbSe<sub>2</sub> has been determined from single-crystal data above and below the transition. At room temperature 2H-NbSe<sub>2</sub> has a layered hexagonal structure with the niobium atoms at the center of trigonal selenium prisms. At the transition the unit cell doubles along the *a* axis. The hexagonal symmetry is conserved and 2/3 of the niobium atoms are displaced from their  $\bar{6}m2$ -point symmetry. The coupling of these niobium atoms seems to be the driving mechanism for the crystallographic distortion.

At room temperature the 2H polytype niobium diselenide, 2H-NbSe<sub>2</sub>, has a layered structure in which each niobium atom is surrounded by six selenium atoms arranged as a trigonal prism and each selenium atom is bonded to three niobium atoms. This structure belongs to space group  $P6_3/mmc$  with *AcABcB* layer sequence. In this notation the capital letters designate the anion sheets while the small letters designate the cation sites. A thorough description of layer structure chalcogenides and their properties has been published by Wilson and Yoffe (1). Lee et al. reported that at  $T \approx 40^\circ\text{K}$ , 2H-NbSe<sub>2</sub> underwent a transition which was characterized by a maximum in the magnetic susceptibility and a sign reversal in the Hall coefficient (2). This anomalous behavior was interpreted as experimental evidence for anti-ferromagnetic ordering. Recent studies of nuclear magnetic resonance of <sup>93</sup>Nb in NbSe<sub>2</sub> by Ehrenfreund et al. (3) have shown that this material is definitely not magnetically ordered below 40°K. Furthermore, these authors reported that the axially symmetric <sup>93</sup>Nb quadrupole powder pattern observed at 77°K and 300°K, was found to be split at 4.2 and 20°K. This suggested that the transition could be accompanied by a structural distortion which would break the hexagonal array of Nb atoms in the layers and that this crystallographic distortion could be responsible for the observed anomalies in the electrical properties. This paper

reports the results of a single-crystal structure determination at 15°K, and the variation of the lattice parameters and the magnetic susceptibility between 5°K and 298°K.

### Experimental

The powder samples of 2H-NbSe<sub>2</sub> were the same as those used in Ref. (3). Single crystals were grown by vapor-transport in a 100° gradient from 1000 to 900°C. Iodine (5 mg/cc) was used as a carrier. The runs were of two weeks duration. Powder finer than 175 mesh was mounted in an MRC cryostat which was aligned in a GE-XRD5 powder diffractometer. Ni-filtered CuK $\alpha$  radiation was used. Complete tracings were taken of three different samples at 298, 77 and  $\sim 5^\circ\text{K}$ . All the patterns could be indexed on a hexagonal cell which proved to be the polytype 2H-NbSe<sub>2</sub>. The preferred orientation was quite pronounced along the direction [001]. As a result of this, three reflections, 10·15, 11·14 and 00·16, were observed in an angular region of  $2\theta$  greater than 147°. These reflections were utilized to determine the variation of the lattice parameters as a function of temperature. An internal silicon standard was used to determine the zero in  $2\theta$  of the diffractometer.

The crystal structure of 2H-NbSe<sub>2</sub> was determined at 298°K and 15°K from single-crystal data collected on a GE-XRD5 diffractometer which was equipped with a single-crystal goniostat, a scintillation counter and a decade scalar. Zr-filtered MoK $\alpha$

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radiation with an  $8^\circ$  take-off angle was used. The sample, which was a small platelet, was mounted on a microgoniometer head with the  $a^*$  parallel to the axis of the head. A Mylar baffle was suspended about the crystal in such a way as to allow complete freedom of motion around the  $\phi$  and  $2\theta$  circles and limited freedom along the  $\chi$  circle. Liquid helium was slowly pumped through a transfer tube and the exiting gas was directed at the crystal through a slot in the Mylar baffle. The temperature was calibrated against the helium head pressure. A gold/iron-Chromel thermocouple in the place of the crystal was used for the calibration. Further details of this low-temperature attachment will be published elsewhere (4).

At both temperatures 22 independent reflections were measured on each side of the platelet. For each reflection the approximate angles  $2\theta$ ,  $\chi$ , and  $\phi$  were set semiautomatically. Once a particular reflection was acquired, each angle was then maximized manually. A tracing of the reflection was taken on a strip-chart recorder at a rate of  $2^\circ/\text{min}$ . The integrated intensity was measured with a planimeter. An infinite-plate absorption correction was applied to the  $00l$  reflections at room temperature since only these reflections were used in the refinement. An empirical absorption correction based on the room-temperature refinement, was applied to all 22 independent reflections at low temperature. The least-squares refinements were carried out by using the ORXLS program. The scattering factor tables were those for neutral atoms (5).  $\Delta f'$  and  $\Delta f''$  were taken from the values reported by Cromer for

Mo $K\alpha$  radiation (6). At room temperature the lattice parameters were measured from a film taken on a 114.6 mm diameter Gandolfi Camera. In this camera the single crystal was rotated in a random manner to produce a Debye Scherrer powder pattern with Cu $K\alpha$  radiation. The sample was the same single crystal used for collecting the intensity data. Magnetic susceptibility measurements were performed in the temperature region from 7°K to 300°K by means of the Faraday method using a Cahn balance.

## Results

Figure 1 shows the magnetic susceptibility data as a function of temperature. In contrast to the data of Lee et al. (2) we did not observe a peak in the susceptibility around 50°K in our samples. The small increase at temperatures below 40°K may be caused by a small amount of a magnetic impurity or could be related to the change in crystal structure. It is not possible to separate these two effects.

The powder diffractometer tracings at 298, 77, 5°K clearly showed that if the  $\sim 40^\circ\text{K}$  transition were accompanied by a crystallographic transition, this transition does not involve a change in crystal symmetry. Given a fixed symmetry, the transition could involve the loss of the center of symmetry or a doubling of the unit cell along the  $a$  and/or the  $c$  axes. All these models were tested during the refinements.

The variation of lattice parameters vs temperature for the three powder samples showed a decrease in

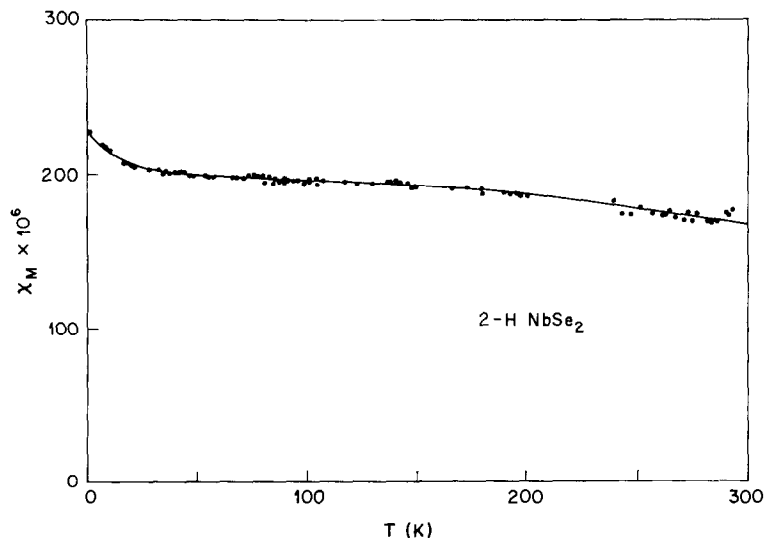


FIG. 1. Molar magnetic susceptibility of 2H-NbSe<sub>2</sub> as a function of temperature.

$c/a$  ratio from a value of 3.642 at 298°K to 3.628 at 5°K. The first sample showed a hysteresis of 80° in the discontinuity of  $c/a$  versus  $T$ . We observed a discontinuous decrease of 0.1% in  $c/a$ . This discontinuity occurred between 77 and 5°K on cooling and at 120°K on warming. For the other two samples a smaller discontinuous decrease was observed but without the hysteresis. The  $\Delta(c/a)$  at the transition was barely above our limit of detectability (0.03%) and an asymptotic curve could fit the data. Both the thermal and mechanical history of the powdered samples were important factors affecting the transition. Also the superconductivity transition appears to be sensitive to small changes in the stoichiometry of the samples (7). The single-crystal data corresponding to the refinements done at 298°K are reported in Table I. The final  $z$ -parameter for the selenium atoms is in good agreement with the value previously reported by Brown and Beerntsen (8). Its standard deviation improved by a factor of 5. The principal interatomic distances are also reported in the same table.

In Tables II and III the crystal data for 2H-NbSe<sub>2</sub> at 15°K are reported. Three models were assumed for the low-temperature structure refinements. The

first model involves the loss of center of symmetry. The space group is  $P6_3mc$ . Two Nb atoms are at  $00\frac{1}{2}$ , two Se atoms are at  $\frac{1}{3}\frac{2}{3}z$  with  $z \sim 0.117$  and the other two at  $\frac{1}{3}\frac{1}{3}z$  with  $z \sim 0.883$ . Convergence was attained after a few cycles of refinement with an  $R = \sum |\Delta F| / \sum |F_0| = 3.1\%$ .

As required by the NMR results our second model contained two types of Nb atoms with different point symmetry. This condition plus the requirement that the crystal symmetry remain hexagonal, led to a unit cell with  $a_{\text{new}} = 2a_{\text{old}}$  and  $c_{\text{new}} = c_{\text{old}}$  in the same group  $P6_3/mmc$ . It was not necessary to double the  $c$  parameter since neither the powder and single-crystal X-ray data, nor the NMR results

TABLE II  
CRYSTAL DATA OF 2H-NbSe<sub>2</sub> AT 15°K

Unit cell with doubled- $a$  lattice parameter

$a = 6.880$  (1) Å  
 $c = 12.482$  (2) Å  
 $c/a = 1.814$   
 Space group  $P6_3/mmc$   
 8 formula weights per unit cell  
 6 Nb in  $x, 2x, \frac{1}{2}$ ;  $x = 0.4967$  (9)  
 2 Nb in  $00\frac{1}{2}$   
 12 Se in  $x, 2x, z$ ;  $x = 0.1678$  (7),  $z = 0.1160$  (2)  
 4 Se in  $\frac{1}{3}, \frac{2}{3}, z$ ;  $z = 0.1178$  (6)  
 Overall temperature factor 0.09 (4)

$h$	$k$	$l$	$F_0$	$F_c$
1	0	3	2	2
2	1	3	6	8
2	1	5	3	3
3	0	7	6	4
3	0	1	7	8
0	0	4	193	194
0	0	6	349	356
0	0	8	523	529
0	0	12	79	78
0	0	14	337	316
0	0	16	288	274
0	0	22	239	237
2	0	0	31	30
4	0	0	18	20
4	4	0	373	382
6	6	0	237	249
2	2	2	167	164
4	4	4	112	107
4	4	2	100	107
4	4	6	204	199
2	2	4	159	157
4	4	8	322	320
2	2	6	292	287
2	2	8	431	449
4	4	16	198	197

TABLE I

CRYSTAL DATA OF 2H-NbSe<sub>2</sub> AT 298°K

$a = 3.4446$  (2)  
 $c = 12.5444$  (7)  
 $c/a = 3.6418$   
 Space group  $P6_3/mmc$   
 2 formula units per unit cell  
 2 Nb in  $0, 0, \frac{1}{2}$   
 4 Se in  $\frac{1}{3}, \frac{2}{3}, z$ , with  $z = 0.1172$  (2)  
 Overall temperature factor = 0.49 (7) Å<sup>2</sup>

$h$	$k$	$l$	$F_0$	$F_c$
0	0	4	46	49
0	0	6	86	85
0	0	8	128	129
0	0	10	5	6
0	0	12	20	20
0	0	14	72	67
0	0	16	63	61
0	0	18	9	9
0	0	22	42	43

$R = \sum |\Delta F| / \sum |F_0| = 3.0\%$

6 Nb-Nb 3.445 Å

6 Nb-Se 2.595 (2) Å

6 Se-Se 3.445 Å in the  $xy$  plane

3 Se-Se 3.333 (5) Å along the  $z$  axis

Se-Se along the octahedral edge 3.549 (5) Å

Vertical separation of sandwiches 2.939 Å

TABLE II—continued

$R = \sum |\Delta F| / \sum |F_0| = 2.8\%$

2 Nb(1)–Nb(2)	3.440 (6) Å	
2 Nb(1)–Nb(1)	3.372 (6) Å	
2 Nb(1)–Nb(1)	3.51 (2) Å	
6 Nb(2)–Nb(1)	3.440 (6) Å	
Nb(1) prism		
2 Nb(1)–Se(2)	2.613 (5) Å	
4 Nb(1)–Se(1)	2.576 (6) Å	
4 Se(2)–Se(1)	3.440 (5) Å	} ~ in the <i>xy</i> plane
2 Se(1)–Se(1)	3.42 (1) Å	
2 Se(1)–Se(1)	3.35 (1) Å	} ~ along the <i>z</i> axis
Se(2)–Se(2)	3.30 (1) Å	
Nb(2) prism		
6 Nb(2)–Se(1)	2.608 (2) Å	
6 Se(1)–Se(1)	3.464 (5) Å	~ in the <i>xy</i> plane
3 Se(1)–Se(1)	3.346 (6) Å	~ along the <i>z</i> axis
Se(1)–Se(2)	3.519 (5) Å	} between two layers
Se(1)–Se(1)	3.522 (5) Å	

Vertical separation of the sandwiches 2.906 Å.

gave experimental evidence for this assumption. Two Nb atoms are in  $00\frac{1}{2}$  with point symmetry  $\bar{6}m2$ , while the remaining six are in  $x, 2x, \frac{1}{2}$  ( $x \sim 0.5$ ) with point symmetry  $mm$ . Four Se atoms are in  $\frac{1}{2}\frac{1}{2}z$  with  $z \sim 0.117$  and the other 12 in  $x, 2x, z$  with  $x \sim \frac{1}{2}$  and  $z \sim 0.117$ . After a few cycles of refinement based on the reflections in common with the smaller cell, structure factors for reflections with odd  $h$  and/or  $k$  were calculated. Of these latter reflections, the ten strongest ones were measured at 15°K. None of their intensities were more than twice the background count. The refinement of the structure was continued including five of these weak reflections. Their assigned intensities were one-half the background count. The final results of this refinement are reported in Table II. A projection of this model on the *xy* plane is shown in fig. 2.

The third model is identical with the room temperature structure. If one excludes the point-symmetry argument resulting from the NMR data, this last model is entirely consistent with our powder and single-crystal X-ray data. For comparison purposes the crystal data corresponding to this last model are reported in Table III.

### Discussion

The acentric model can be discarded since the selenium *z*-coordinates are centrosymmetrically related plus or minus one standard deviation. Secondly, the *R* factor is identical to the centrosymmetrical model. And thirdly, the acentric space group is not compatible with the NMR results. The only significant difference between the second

TABLE III  
CRYSTAL DATA OF NbSe<sub>2</sub> AT 15°K

Same unit cell as room temperature				
$a = 3.440 (1)$				
$c = 12.482 (2)$				
$c/a = 3.628$				
Space group $P6_3/mmc$				
2 formula units per unit cell				
2 Nb in $00\frac{1}{2}$				
4 Se in $\frac{1}{2}\frac{1}{2}z$ ; $z = 0.1163 (2)$				
Overall temperature factor = 0.10 (4) Å <sup>2</sup>				
<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>0</sub>	<i>F</i> <sub>c</sub>
0	0	4	48	49
0	0	6	87	90
0	0	8	130	132
0	0	12	20	19
0	0	14	87	79
0	0	16	71	68
0	0	22	59	59
1	0	0	8	8
2	0	0	4	5
2	2	0	93	96
3	3	0	59	63
1	1	2	41	41
2	2	4	28	26
2	2	2	25	27
2	2	6	51	50
1	1	4	39	39
2	2	8	80	80
1	1	6	72	72
1	1	8	107	112
2	2	16	49	49

$R = \sum |\Delta F| / \sum |F_0| = 3.1\%$

6 Nb–Nb	3.440 Å
6 Nb–Se	2.593 (2) Å
6 Se–Se	3.440 Å in the <i>xy</i> plane
Se–Se	3.337 (5) Å along the <i>z</i> axis
Se–Se	between two layers 3.518 (5) Å
Vertical Separation of Layers 2.904 Å	

and the third models is the displacement of  $\frac{1}{3}$  of the niobium atoms in the *xy* plane. This displacement is 3.7 times one standard deviation. The *R* factor for the second model is 2.8% as against 3.1% for the third model. In addition, the second model is commensurate with the NMR results, whereas the third model is not. Another possibility which would be consistent with the X-ray and NMR data involves the loss of the hexagonal crystal symmetry. However, careful scans of the three back-reflection peaks (with  $2\theta > 147$ ) showed no line broadening. From the machine settings we estimated that there was no change in crystal symmetry within 1/30,000. A

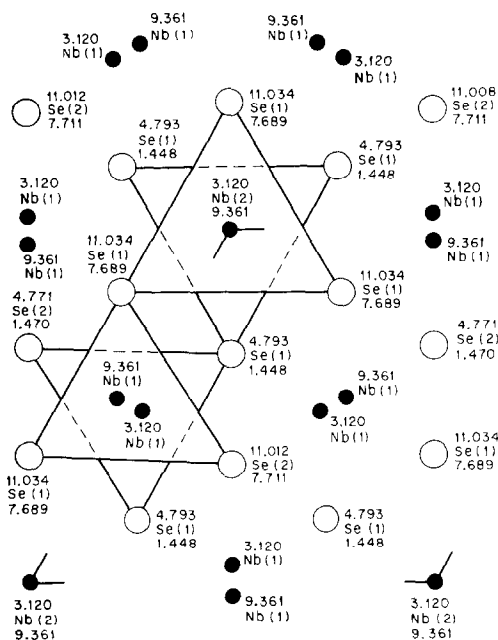


FIG. 2. A projection of the double- $a$  low-temperature structure of  $2H$ -NbSe<sub>2</sub> on the  $xy$  plane. The heights of the atoms are given in angstroms, and the Nb(1) displacements have been exaggerated for clarity.

distortion less than this limit could not explain the splittings in the NMR spectra.

The six equal Nb–Se distances in the trigonal prism at room temperature are 2.595 Å. The prism edges in the basal plane are 3.445 Å or 3.3% larger than the edges along the  $z$ -axis which are 3.333 Å. The vertical separation of sandwiches is 2.939 Å. Each Nb atom has six equidistant Nb neighbors at 3.445 Å in the basal plane. At 15°K in the double- $a$  structure there are two independent Nb sites. The Nb(1) atom moves out of the point symmetry  $\bar{6}m2$  toward a prism face. As a consequence of this displacement this face elongates along the  $z$ -axis and contracts in the basal plane. The remaining vertical edge of the prism contracts. There are two Nb–Se distances of 2.613 Å and four of 2.576 Å, the

average being 2.588 Å. The Nb(2) atoms remain in the same point symmetry at the body center of the prism. The six Nb–Se distances are 2.608 Å. This value is slightly larger than the room temperature value of 2.595 Å. The overall average Nb–Se distance at 15°K remains 2.595 Å. The vertical separation of sandwiches at 15°K is 2.906 Å which is 1.1% smaller than the room temperature value of 2.939 Å. However, the  $c$  parameter decreases only 0.5% from 298 to 15°K, since the average height of the sandwiches increases slightly along the vertical axis. At 15°K for Nb(2) the six equidistant Nb neighbors are at 3.440 Å as against 3.445 Å at room temperature. For Nb(1) there are two neighbors at 3.440 Å, two at 3.372 Å, and two at 3.51 Å.

We believe that the coupling of the Nb(1) atoms could be the motivating cause for the crystallographic distortion at 40°K. Certainly the anomalous contraction of the empty Se-octahedra and the smaller decrease in the  $c/a$  ratio cannot be explained in terms of normal thermal effects.

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