Structural behaviour of NiS₂ up to 54 kbar

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Abstract

Single-crystal X-ray diffraction experiments were carried out on NiS₂ under high pressures with the aid of a diamond-anvil cell. The pressure dependence of the *a* dimension was found to be linear over the experimental pressure range across the transition point with a good approximation. The S-S bond length is practically constant up to the transition pressure and decreases rapidly above it. The Ni-S length decreases with pressure both in the semiconductor and metallic phases within the pressure range of this experiment. However, the decrement is slower in the higher pressure, metallic phase than in the semiconductor phase. Discontinuities in the plots of bond lengths against pressure are not so large as can be recognized with the precision of this experiment.

Introduction

Crystals of NiS₂ have a pyrite-type structure with the cubic symmetry of space group Pa3. It is known that the crystals show a phase transition at about 46 kbar under room temperature from a low pressure, semiconductor phase to a high pressure, metallic phase (Mori *et al.*, 1981). Endo *et al.* (1973) examined the cell dimensions up to 105 kbar with the powder X-ray diffractometry, and found discontinuity in the compressibility of the cell volume at the transition point. Further, the latter authors reported that no significant changes were observed in intensities on passing through the phase transition pressure, suggesting a non-reconstructive change at the transition point. A study with Raman spectroscopy was carried out on NiS₂ under high pressure by Takahashi *et al.* (1985), revealing a frequency shift in the A_g mode of the S₂ group at the transition point. Since this result indicates a change of the S-S bond strength on the phase transition, the bond length and its dependence on pressure are expected to change at the transition point. The present authors carried out the single-crystal X-ray diffraction experiments on NiS₂ with the aid of a diamond-anvil cell to obtain detailed information on these points.

In the previous paper (Fujii *et al.*, 1986) structure changes of FeS₂ and CoS₂ under high pressure have been reported. The results of the present study will be com-

pared with those of FeS₂ and CoS₂.

Experimental

Single crystals used in this study were grown from the powders of NiS₂ synthesized by direct reaction of metallic nickel and sulphur at 770°C with Prior's method (Prior, 1961). A crystal with dimensions 0.10 × 0.10 × 0.04 mm was selected for X-ray diffraction experiments. The diamond-anvil cell designed by Miyake *et al.* (1982) was used for the high-pressure diffraction experiments. The crystal was put into the hole (0.3 mm in diameter) of the gasket (SUS631) together with a piece of ruby crystal for pressure calibration (Piermarini *et al.*, 1975), and stuck on a culet face of a diamond crystal by grease. A 4:1 methanol-ethanol mixture was used for the pressure transmitting medium (Piermarini *et al.*, 1973; Finger & King, 1978).

Cell dimensions under the relevant pressures (32, 49 and 54 kbar) were determined from 2θ values of 25 reflections in the range of $35^\circ < 2\theta < 46^\circ$ for Ag K α radiation by the least-squares method. The obtained values are given in Table 1. The space group Pa3 was confirmed from the Laue symmetry and the extinction rules of reflections on Weissenberg photographs under ambient pressure.

Intensity measurements were carried out on a Rigaku automated four-circle diffractometer at 32, 49 and 54 kbar under room temperature. Ag K α radiation monochromatized with pyrolytic graphite was used for the measurements. Centering of the crystal was performed with the method reported by King and Finger (1979). After the orientation of the crystal was determined, the holes of hemispherical beryllium windows (Miyake *et al.*, 1982) were filled with beryllium rods, so that the beryllium windows form perfect hemispheres and give equal absorption effects for every reflections.

Intensity data were collected in the fixed ϕ mode (Finger & King, 1978) with a control program developed by Fujii and Marumo (1986). A rather slow scan speed of 1°/min in θ was adopted to accumulate reasonable counts for respective reflections. Although the open angle of the window of the cell was 90°, it was found that several

TABLE 1. Crystal data of NiS₂. The result at 1 bar is quoted from that reported by Sato and Noda (1983).

Space group	Pa3
Cell dimension a (Å)	
1 bar	5.6845(4)*
32 kbar	5.6196(6)
49 kbar	5.5852(4)
54 kbar	5.5745(4)
Z	4
D_x at 1 bar (g/cm ³)	4.451
$\mu(\text{AgK}\alpha)$ at 1 bar (cm ⁻¹)	62.5

reflections in the higher angle range were hidden by the gasket or by the steel base of the cell, even when the 2θ angles were lower than 90° . Therefore, reflections with 2θ angles less than 80° were measured. The ω -scan mode was adopted in the region of $0^\circ < 2\theta \leq 40^\circ$, whereas the 2θ - ω scan mode was employed in the higher angle region. For all reflections, peak profiles were recorded to check overlapping with reflections from diamond or beryllium, and shadowing by the steel base of the high-pressure device.

Although most of strong powder lines of beryllium exist in the region of $2\theta \leq 40^\circ$ for Ag $K\alpha$ radiation, it was revealed that several reflections were overlapping with beryllium powder lines in the higher angle region where the 2θ - ω scan mode was adopted. These reflections were distinguished from the 2θ angles and the shapes of peak profiles, and deleted from the data sets together with those overlapping with diamond reflections and those partially cut by the gasket or by the edge of steel base. Details of the procedure to identify the partially cut reflections is given in the previous paper (Fujii *et al.*, 1986).

The observed intensities were corrected for the Lorentz, polarization and absorption factors. The absorptions due to the diamond crystals were corrected after the method reported by Finger & King (1978). Finally, 528, 473 and 480 reflection data with $|F_o| \geq 3\sigma(|F_o|)$ were obtained in the measurements under 32, 49 and 54 kbar respectively, and used for structure refinements. Here, $\sigma(|F_o|)$ is the standard deviation of the observed structure amplitude $|F_o|$ due to the counting statistics. The numbers of crystallographically independent reflections are 90, 85 and 84, respectively.

Structure refinements

In all the structure refinements, equivalent reflections were not averaged, and treated as independent reflection data. Refinements were carried out with a full-matrix least-squares program LINKT85, starting from the final atomic parameters of NiS_2 under room pressure reported by Sato and Noda (1983). In the first cycle of refinements, only a scale factor was varied, and then one positional parameter of S, anisotropic temperature factors of Ni and S, anisotropic secondary extinction correction parameters (Becker & Coppens, 1974) were varied together with the scale factor. The final weighted discrepancy factors R_w were 0.043, 0.046 and 0.054 for data of 32, 49 and 54 kbar, respectively. The quantity minimized was $\sum (|F_o| - k|F_c|)^2$. Atomic scattering factors for neutral atoms and anomalous dispersion factors were taken from International Tables for X-Ray Crystallography (1974). The final atomic parameters are given in Table 2. Refinements were also carried out after averaging equivalent reflections. However, no significant differences were observed

TABLE 2. The final atomic parameters of NiS₂ at 1 bar and under high pressures. The temperature factors are the coefficients in the expression $\exp [-(2\pi^2/a^2) U_{11}(h^2 + k^2 + l^2) + 2U_{12}(kl + lh + hk)]$. The equivalent isotropic temperature factors are given as $B_{eq} = 8\pi^2(U_{11} + 2U_{12})$. Results at 1 bar are quoted from those reported by Sato and Noda (1983).

	1 bar	32 kbar	49 kbar	54 kbar
x	0.39470(1)	0.3938(1)	0.3935(2)	0.3939(2)
U_{11} (Ni)	0.00603(3)	0.0068(2)	0.0060(2)	0.0066(3)
U_{11} (S)	0.00017(1)	0.0000(3)	-0.0005(3)	0.0002(4)
U_{12} (S)	0.00534(1)	0.0051(2)	0.0054(3)	0.0056(4)
U_{11}^{12} (S)	-0.00023(2)	-0.0002(3)	-0.0003(3)	-0.0024(4)
B_{eq} (Ni)	0.503	0.54	0.39	0.55
B_{eq} (S)	0.385	0.37	0.38	0.06

Ni : (0,0,0), S : (x, x, x)

$U_{11} = U_{22} = U_{33}$ and $U_{12} = U_{23} = U_{13}$ for both Ni and S.

between the obtained parameters and those in Table 2.

A list of observed and calculated structure factors may be obtained upon request from Research Laboratory of Engineering Materials, Tokyo Institute of Technology.

Results and discussion

The interatomic distances and bond angles under respective pressures are given in Table 3. In the pyrite-type structures, metal atoms locate at (0, 0, 0), and sulphur atoms occupy (x, x, x) in the space group Pa3. Two sulphur atoms at (x, x, x) and (1-x, 1-x, 1-x) are considered to form an S₂ molecule with a fairly short distance of about 2.1 Å. The Ni atoms have trigonally deformed octahedral coordinations by S atoms. Each S atom forms one S-S and three Ni-S bonds disposed tetrahedrally.

The a dimension is plotted against pressure in Fig. 1. It has been generally accepted that insulator-metal transitions are of first order. It is of interest that the gap at the transition point is so small in NiS₂ as seen in Fig. 1 that the four observed points are on a straight line within the experimental errors.

The pressure dependence of the individual bond lengths are shown in Fig. 2. The Ni-S bond length reduces with increasing pressure through out the pressure range of

TABLE 3. The bond distances (Å) and bond angles (°) in NiS₂ at 1 bar and under high pressures. Results at 1 bar are quoted from those reported by Sato and Noda (1983).

	S-S	Ni-S	S-Ni-S	Ni-S-S	Ni-S-Ni
1 bar	2.0735(1)	2.3981(1)	93.572(2) & 86.428(2)	104.594(3)	113.877(2)
32 kbar	2.068(2)	2.368(1)	93.64(2) & 86.36(2)	104.38(3)	114.05(3)
49 kbar	2.061(3)	2.353(1)	93.66(3) & 86.34(3)	104.32(4)	114.10(3)
54 kbar	2.050(3)	2.350(2)	93.64(3) & 86.36(3)	104.40(5)	114.03(4)

FIG. 1. Pressure dependence of the cell dimension of NiS_2 .

this experiment, whereas the S-S length is practically constant up to the transition pressure and decreases rapidly above it. Decrement of the Ni-S length is smaller above the transition pressure than below it. These facts suggest that the S-S bond is softened and the Ni-S bond is hardened on the phase transition from semiconductor to the metallic phase. As seen in Fig. 2, gaps of bond lengths at the transition point are not so large as can be recognized with the accuracy of this experiment.

Transition metals have the low-spin configurations in pyrite-type crystals as indicated by the magnetic susceptibilities (Burns, 1970). In the low-spin state, an Fe^{2+} ion in an octahedral field has no electron in the d_y orbitals, whereas a Co^{2+} ion has one electron in it. An Ni^{2+} ion in an octahedral field has only one possible configuration in the ground state, having two electrons in the d_y orbitals. The S-S bond in CoS_2 (2.11 Å) is much shorter than that in FeS_2 (2.16 Å) (but still larger than the S-S bonds in S_6 and S_8 molecules) and the decrement of the S-S length with increasing pressure is much smaller in the former crystal than in the latter. This difference is supposed to be caused by the difference in the configuration of 3d electrons. The results of the present study on the semiconductor phase lies on the same line as seen in these two crystals. Namely, the S-S length in NiS_2 , where two electrons occupy the d_y orbitals, is shorter than that in CoS_2 , where only one electron exists on the d_y orbitals, and practically constant with the variation of pressure up to the transition point. On the other hand, the short S-S distance and its rapid decrease just above the transition

FIG. 2. Pressure dependence of bond lengths in NiS_2 .

pressure are interesting observations. These results are expected to give important information on the mechanism of the phase transition. We need, however, more precise experiments to establish the structural behaviour of the crystal under the higher pressure range.

Acknowledgments—The authors thank Professor Syun-iti Akimoto and Dr. Toshihiro Suzuki in Institute for Solid State Physics, The University of Tokyo for their help and generous permission in using pressure calibration system. They also thank Professor Setsuro Asano of Faculty of Education, The University of Tokyo for his valuable discussions.

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Received August 22, 1986; revised May 11, 1987.