CHEMISTRY

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1962

SovietRxiv

Figure 2. Line diagram of a preparation of composition NbS3

Figure 1: Figure 2. Line diagram of a preparation of composition NbS3

Abstract

Full Text

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STUDY OF NIOBIUM SULFIDES

Niobium sulfides were studied by Biltz and Kocher ([1]) and later by Hegg and Schönberg ([2,3]). In work ([1]), niobium sulfides were prepared by heating niobium with sulfur. By tensimetric measurements and X-ray examination the authors discovered the compound Nb_2S_3, which dissolves sulfur up to the composition NbS_4, and the compound NbS, which dissolves niobium up to the composition $NbS_{0.5}$. Hegg and Schönberg ([2]) prepared niobium sulfides by heating powders of niobium and sulfur in evacuated ampoules, and also by passing carbon disulfide over heated niobium. The authors found two phases, NbS_2 and NbS, with narrow homogeneity ranges, the limits of which they did not determine. The phase

Fig. 2. Line diagram of a preparation of composition NbS_3 (very weak lines are not included).
1—Crystals obtained at the top of the ampoule (I), obtained on the surface of the preparation (II), main mass (III)

NbS_2 crystallizes in a lattice similar to $CdCl_2$, while NbS changes from the WC type (with an excess of niobium relative to the composition $1:1$) to the NiAs type (with an excess of sulfur relative to the composition $1:1$). The electrical properties of niobium sulfides were not studied by the above-mentioned authors.

We previously studied the electrical properties of niobium selenides and tellurides; it was of interest to investigate the electrical properties of niobium sulfides. To obtain niobium sulfides we used metallic niobium containing 99.8% Nb (impurities Fe, Al, Ta, Si), which before use was annealed at 1600° in vacuum (10^{-4} mm Hg) under continuous pumping until gas evolution ceased. The sulfur was purified by repeated recrystallization from carbon disulfide (chemically pure grade) and by repeated distillation in vacuum.

The preparations were obtained by prolonged (1000 h) annealing of calculated amounts of niobium and sulfur in evacuated (10^{-4} mm Hg) quartz ampoules at 550°, followed by slow stepwise cooling to 20° over 1000 h. Preparations contain-

Fig. 3

Figure 2: Fig. 3

Fig. 4

Figure 3: Fig. 4

ing up to 50 at.% sulfur appeared as homogeneous black powders; preparations with a higher sulfur content were black sintered masses. The preparation that co-

contained 75 at. % sulfur, was obtained in the form of a soft mass possessing lubricating properties. Under the microscope, threadlike crystallites were visible in it; at the top of the ampoule, well-formed needle crystals were obtained. The same crystals also formed on the surface of the main mass of the substance located in the lower part of the ampoule (Fig. 1, see insert, p. 774).

Fig. 3. Dependence of the specific electrical conductivity (a) and thermoelectromotive forces (b) on composition in the niobium–sulfur system (a)

Separately taken crystals of the preparation of composition NbS_3, obtained at the top of the ampoule, on the surface of the preparation, and also from its main mass, gave completely identical powder diagrams (Fig. 2). This indicates the single-phase nature of the preparation of composition 1 : 3. We did not determine the homogeneity limits of this phase. X-ray investigation of the preparations was carried out with copper radiation by the powder method. An RKD camera (diameter 57.3 mm) was used. The intensity of the diffraction lines was estimated visually on a ten-point scale.

From the niobium sulfides obtained, cylindrical pellets were prepared for measurements of electrical conductivity and thermoelectromotive force.

The method of preparing specimens for measuring their electrical properties was described by us earlier ([4]). The results of measurements of specific electrical conductivity and thermoelectromotive force are given in Fig. 3.

Fig. 4. Dependence of the specific electrical conductivity of niobium trisulfide on temperature

The numerical values of the electrical conductivity of preparations containing up to 70 at. % sulfur indicate the semimetallic character of the bonding in them. A preparation of composition NbS_3, pressed under a pressure of 13,000 kg/cm^2, has at 20° a specific electrical conductivity equal to $1.5 \cdot 10^{-4}\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$, and a thermoelectromotive-force coefficient equal to 500 μV/deg relative to aluminum.

For measuring the temperature dependence of the electrical conductivity and Hall effect of a preparation of composition NbS_3, a specimen was made from it by pressing a rectangular plate 1 mm thick with contacts pressed into it. The electrical conductivity of this specimen increases strongly with increasing tem-

temperature. Figure 4 shows the dependence of the logarithm of the specific electrical conductivity on $1/T$.*

It was not possible to measure the Hall effect, since its magnitude was within the measurement error in the temperature range from $-178°$ to $+45°$, which indicates an extremely low mobility of current carriers in niobium trisulfide.

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Received
27 II 1962

REFERENCES

1. W. Biltz, A. Köcher, *Zs. anorg. Chem.*, **237**, 369 (1938).
2. G. Hägg, N. Schönberg, *Arkiv Kemi*, **7**, 371 (1954).
3. N. Schönberg, *Acta metallurgica*, **2**, 427 (1954).
4. A. V. Novoselova, L. A. Grigoryan, Yu. P. Simanov, *DAN*, **135**, 864 (1960).

* The authors express their gratitude to V. V. Ostroborodova for assistance in measuring the temperature dependence of the electrical conductivity.

Note: Figure translations are in progress. See original paper for figures.