

LETTER TO THE EDITOR

Anisotropy in the resistivity of NbSe₂ with pressure

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Abstract. The anisotropy in resistivity of NbSe₂ decreases with pressure, reaching a value of about five at 45 kb. A crystallographic phase change occurs at a pressure of 33 ± 3 kb.

NbSe₂ is a metal belonging to the family of transition metal dichalcogenides which form layer-type crystals: details of the crystallography may be found in the review by Wilson and Yoffe (1969) together with a simple energy band scheme. In this band model the uppermost valence band, made up from the d_{z²} orbitals of the Nb atoms, is only half full, thus accounting for the metallic properties of NbSe₂. The most common polytype of NbSe₂ is the two layer, or 2H modification where the Nb atoms in neighbouring layers are directly above one another in the *c* direction. Because of the weak interlayer forces a relatively large increase in the interlayer Nb-Nb overlap is expected under pressure. There has been recent interest in the rapid increase of the superconducting transition temperature with pressure (Jerome *et al* 1971, Jones *et al* 1972). We report here on the behaviour of the resistivity of the 2H form of NbSe₂ under pressure.

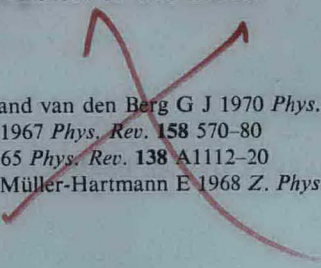
The $\rho_{\perp c}$ (along the layers) was measured using a standard four-probe technique with silver-dag contacts. For measurements of $\rho_{\parallel c}$, the technique of Edwards and Frindt (1971) was used: this involves small voltage probes partially cleaved from the body of the crystal. The samples used were hexagonal platelets typically 1 to 2 mm across with thicknesses of the order of 0.15 mm for $\rho_{\parallel c}$ and 0.05 mm for $\rho_{\perp c}$.

Two types of apparatus were used for high pressure measurements. Hydrostatic pressures up to 15 kb were applied in a piston and cylinder apparatus (Pitt and Gunn 1970) using a 50:50 mixture of amyl alcohol and castor oil as the pressure transmitting medium. Here only slight hysteresis was observed and the sample resistivity returned to its original value for both orientations when the load was removed. Pressure measurements to 100 kb were made using a Bridgman anvil apparatus described by Pitt (1968): the crystal was potted in epoxy resin at the centre of a MgO-loaded epoxy ring.

The behaviour of the resistivity perpendicular to the crystal *c* axis with pressure at room temperature is shown in figure 1. After an initial decrease, $\rho/\rho_0(\perp c)$ tends to level off until another decrease is observed at about 30 kb. Here ρ_0 corresponds to the resistivity at atmospheric pressure. A much greater effect is observed for $\rho/\rho_0(\parallel c)$, also shown in figure 1. Here $\rho_{\parallel c}$ is decreased to $\frac{1}{10}$ of its atmospheric pressure value at a pressure of 45 kb. As shown in the figure 1 inset, the anisotropy in resistivity $\rho_{\parallel c}/\rho_{\perp c}$ decreases with

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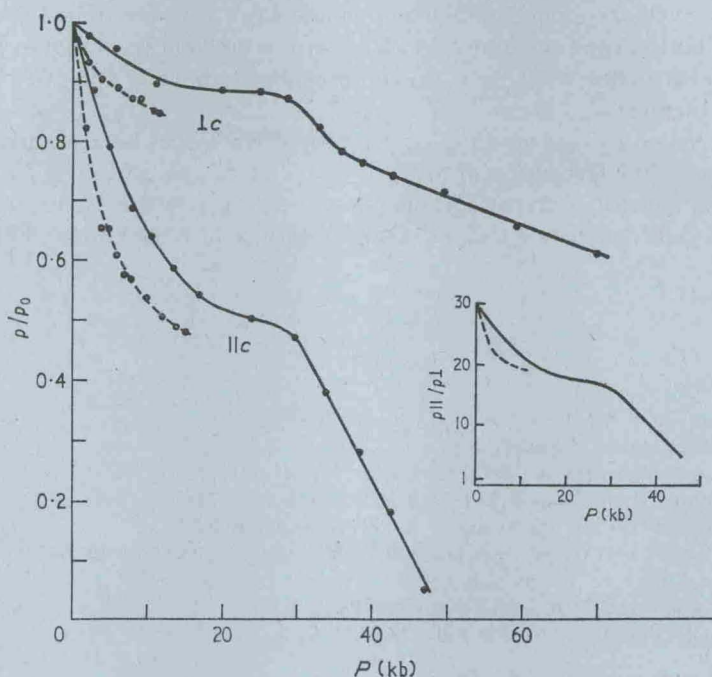


Figure 1. The relative resistivity $\perp c$ and $\parallel c$ for NbSe₂ as a function of pressure at room temperature. Inset: anisotropy in resistivity of NbSe₂. Full lines, Bridgman anvil apparatus; broken lines, reversible hysterostatic runs.

pressure and drops to about 5 at 45 kb. We have taken $\rho_{\parallel c}/\rho_{\perp c}$ to be 30 at atmospheric pressure (Edwards and Frindt 1971). No corrections have been made for changes in sample dimensions.

The temperature dependence of $\rho_{\perp c}$ down to 85K was measured at 31 kb and 70 kb. The results are basically similar to the atmospheric pressure results of Lee *et al* (1969). Lee *et al* observed a small change in the slope of ρ against T at about 145K; this is known not to be a phase change. At 31 kb the change in slope appears to be at about 110K, and at 70 kb no slope change is observed.

It was suspected that the 'knee' in both ρ curves may be due to a phase change, and an accompanying change in volume. To investigate this a variation of the manganin gauge technique of Giardini and Samara (1965) was used to follow the volume decrease through the transition. The results show that a volume change starts at 33 ± 3 kb. The volume change is gradual, with a width of about 4 kb. We estimate that the change in volume is less than 2%.

We have also measured $\rho_{\perp c}$ for 2H-TaSe₂ under pressure at room temperature and find that unlike NbSe₂, $\rho/\rho_0(\perp c)$ decreases linearly to 0.75 at 70 kb.

The large initial decrease in $\rho/\rho_0(\parallel c)$ and in the resistivity anisotropy for NbSe₂ may primarily be due to increased interlayer Nb-Nb overlap which tends to level off around 25 to 30 kb. Using the compressibilities given in the literature (Flack 1972, Jones *et al* 1972), the spacing between the Nb planes has changed by 3 to 5% at 30 kb (and the a spacing by 0.5 to 1%). The second resistivity drop is associated with the volume change at 33 kb. It is possible that at 33 kb the crystal goes from the trigonal coordination to the octahedrally coordinated 1s CdI₂ structure (see p 189, Wilson and Yoffe 1969), or to

some other polymorph, but careful high pressure x ray work is required here. The rate of decrease in both ρ_{\parallel} and ρ_{\perp} above 33 kb is not too different from that at low pressures. This may in part reflect a change in the compressibility above 33 kb as well as a change in the band structure.

The superconducting transition temperature of NbSe₂ has been observed to increase linearly up to 17 kb (Jerome *et al* 1971). It would be of interest to see if T_c continues to increase with increasing pressure in the region where the resistivity flattens, and also to determine whether the new (possibly octahedral) form of NbSe₂ above 33 kb is a superconductor.

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