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Optical Studies of Metal-Semiconductor Transmutations Produced by Intercalation

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Abstract. Spectra of the alkali metal intercalation products of MoS₂ and NbSe₂ are interpreted in terms of a previously published band model.

Studies on the intercalation of the layer type transition metal dichalcogenides with metals and organic materials are of particular interest in connection with the superconducting properties of the more metallic members of this set of compounds. Thus pyridine molecules have been successfully introduced between the sandwiches in niobium and tantalum disulphides and diselenides, and from electrical measurements it is concluded that superconductivity may take place in two dimensions along the sheets (Gamble et al. 1970). The first series transition metals have also been incorporated during vapour transport of NbSe₂ etc. into the vacant sites within the van der Waals gap, and some of these products show ordered magnetic states at low temperatures (Anzenhofer et al. 1970, Voorhoeve and Robbins 1970, Hulliger and Pobitschka 1970).

This note is concerned with the optical properties of single crystals of MoS₂ and NbSe₂ containing sodium intercalated from liquid ammonia. There is already a good deal of structural work on such systems (Rudorff 1965, Omlor and Jellinek 1970). The results obtained from optical measurements can be interpreted in terms of the band model recently developed in publications from this laboratory (for example, Wilson and Yoffe, 1969).

Very thin crystals of MoS₂ and NbSe₂ about 1000 Å thick were fixed on the window of a small optical cell. The sodium was intercalated between the sandwiches of these small crystals using a refined vacuum microtechnique.† First a film of solid ammonia was deposited onto the crystal, held at <-78°C, this being followed by a film of metallic sodium of controlled thickness, produced by directing a beam of sodium atoms onto the cooled crystal. With suitable warming and washing procedures it was possible to progressively 'saturate' the crystal with sodium. The optical absorption spectrum was measured for each sodium concentration in the cell used to prepare the specimen. An absolute measure of the amount of sodium incorporated was not made.

The results for the optical absorption spectra at 77 K are given in figures 1 and 2. Figure 1 (a) shows the spectrum of the pure MoS₂ crystal, and figures 1 (b) and (c) are spectra for the intercalated crystal, containing a small (1 to 10% of saturation limit) and a saturated concentration of sodium respectively. It should be noted that the addition of a small amount of sodium (figure 1 (b)) altered the structures C, D and those at higher photon energies more markedly than the exciton peaks A, B; while a saturating concentration of sodium (figure 1 (c)) eventually reduced the intensity of all the absorption peaks and gave rise to the characteristic free carrier absorption on the long wavelength side of the absorption edge (>1μm), as for the metal NbSe₂ (figure 2 (a)). On intercalation of NbSe₂ with sodium a peak in optical absorption appears on the main absorption edge, and the onset of free carrier absorption moves to longer wavelengths. Indeed the spectrum begins to resemble that found for the semiconductors of the MoS₂ family - particularly if made p-type by doping with Nb (see Wilson and Yoffe, 1969, p. 284). If air or water vapour is gradually added to the cell containing the pure material, it is assumed that electrons are ejected from the metal into the conduction band via the band edge.

† For the handling of sodium ammonia solutions see Acrivos and Pitzer (1962).

Figure 1. Optical absorption spectra.

(a), pure crystal (c), same crystal shifted to aid comparison of band edge.

vapour is gradually added to the cell containing the pure material.
Conclusions

Metal dichalcogenides with suitable properties may be compared with the superconducting compounds. Thus pyridine sandwiches in niobium and molybdenum are very fine in this respect (Gamble et al. 1970). The measurements of this paper are directly measurable during vapour transport and, indeed, some of these metals can be obtained in a high degree of perfection (Anzenhofer et al. 1970). Thus, crystals of MoS₂ and NbSe₂ are already a good deal of interest for condensed matter research.

The results obtained on the band model recently described by Gamble and Yoffe (1969) show that if the sandwiched layers are fixed on the window of the spectrometer, the crystals of these small sandwiches of small sheets of solid ammonia was found to be covered by a film of metallic sodium. Indeed, the sodium atoms ionised in situ to Na⁺ and Na⁺, donating mobile electrons into the sandwiches, thus explaining the experimental results in terms of the rigid band model mentioned in the introduction and illustrated in figure 3.

Vapour is gradually admitted into the cell, the sodium reacts and the spectra revert to those of the pure materials, showing the reversibility of the intercalation processes. If it is assumed that the sodium atoms are ionised in situ, then the intercalation processes can be explained by the rigid band model mentioned in the introduction and illustrated in figure 3.

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Figure 1. Electronic absorption spectra of cleaved single crystals of MoS₂ at 77 K. (a), pure crystal; (b), same crystal intercalated with Na (1 to 10% of saturation limit); (c), same crystal intercalated with Na to saturation limit. Curves have been vertically shifted to aid clarity and the absorption coefficients are of order of 10⁸-10⁹ cm⁻¹ above the band edge.

Figure 2. Electronic absorption spectra of cleaved single crystals of NbSe₂ at 77 K. (a), pure crystal; (b), same crystal intercalated with Na to saturation limit. Absorption coefficients are of order of 10⁵ cm⁻¹ above the band edge.

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For MoS₂, the donated electrons go into the otherwise empty conduction band based on the dₓ²-y², dₓy orbitals and a metal is formed with the characteristic spectrum shown in figure 1 (c). The magnetic behaviour changes accordingly from diamagnetism to Pauli paramagnetism (Rudorff 1965). For NbSe₂, the extra electrons are introduced into the half filled band based on the dₓ² orbital, steadily filling that band. For a fully intercalated crystal, namely NaNbSe₂, the dₓ² band would be complete, the result being a semiconductor akin to MoSe₂.

It is intended to make these measurements more quantitative, and also to extend the experiments to include esr, nmr, magnetic, and superconductivity studies.

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RUDORFF, W., 1965, Chimia, 19, 489.

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