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Optical Studies of Metal- Semiconductor Transmutations Produced by Intercalation

Juana Vivó Acrivos
San Jose State University, juana.acrivos@sjsu.edu

Y. Liang
San Jose State University

J. Wilson
San Jose State University

A. Yoffe
San Jose State University

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Abstract. Spectra of the alkali metal intercalation products of MoS_2 and $NbSe_2$ 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 $NbSe_2$ 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 MoS_2 and $NbSe_2$ containing sodium intercalated from liquid ammonia. There is already a good deal of structural work on such systems (Rudorff 1965, Omloo 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 MoS_2 and $NbSe_2$ about 1 000 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 MoS_2 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 ($>1\mu m$), as for the metal $NbSe_2$ (figure 2 (*a*)). On intercalation of $NbSe_2$ 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 MoS_2 family – particularly if made p-type by doping with Nb (see Wilson and Yoffe, 1969, p. 284). If air or water

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

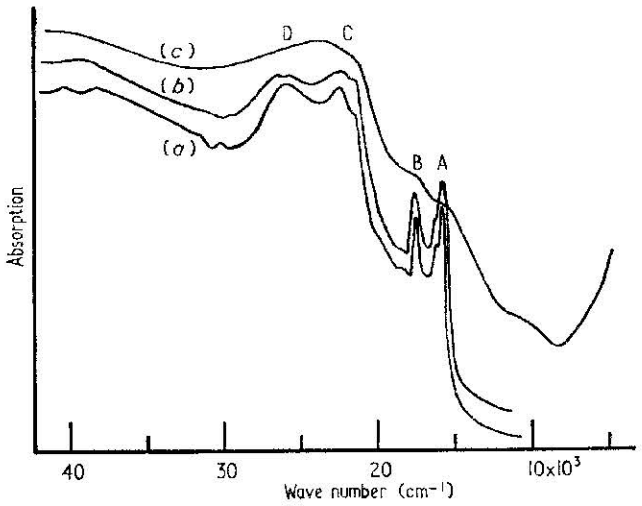

Figure 1. Electronic absorption spectra of cleaved single crystals of MoS_2 at 77 K. (*a*), pure crystal; (*b*), same crystal intercalated with Na (1 to 10% of saturation limit); (*c*), same crystal intercalated with Na to saturation limit. Curves have been vertically shifted to aid clarity and the absorption coefficients are of order of 10^5–10^6 cm^{-1} above the band edge.

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* $Na \rightarrow Na^+ + e$, donating mobile electrons into the *X*–M–*X* sandwiches,† it is possible to explain the experimental results in terms of the rigid band model mentioned in the introduction and illustrated in figure 3.

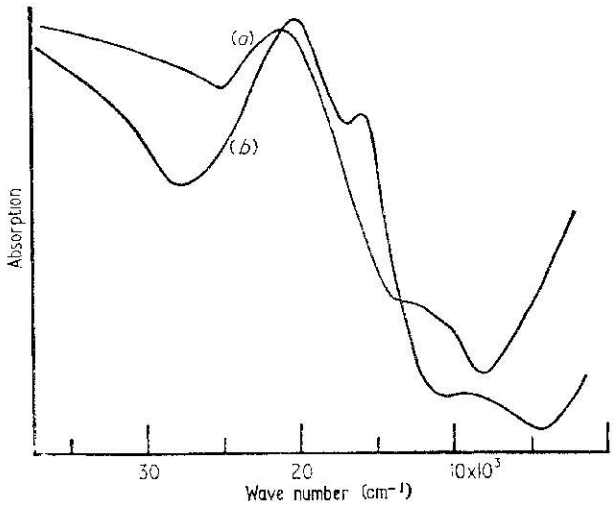

Figure 2. Electronic absorption spectra of cleaved single crystals of $NbSe_2$ at 77 K. (*a*), pure crystal; (*b*), same crystal intercalated with Na to saturation limit. Absorption coefficients are of order of 10^5–10^6 cm^{-1} above the band edge.

† Cf. tungsten 'bronzes', for example, Na_xWO_3–see Advances in Chemistry, *Non-Stoichiometric Compounds*, 1962 *Am. Chem. Soc.*,, **39**, pp. 224 ff.

For MoS_2, the donated electrons go into the otherwise empty conduction band based on the $d_{x^2-y^2}$, d_{xy} 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 $NbSe_2$, the extra electrons are introduced into the half filled band based on the d_{z^2} orbital, steadily filling that band. For a fully intercalated

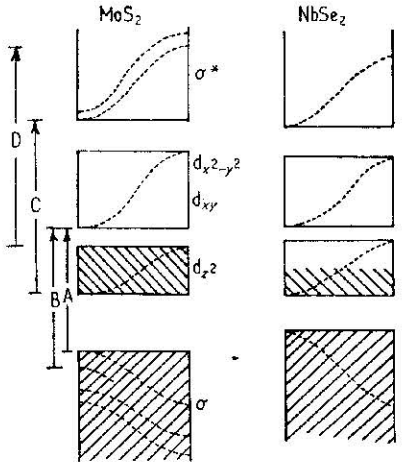

Figure 3. Energy band schemes for MoS_2 and $NbSe_2$. Shaded area represents occupied states and the assignment for A, B, C and D transitions in MoS_2 has been indicated.

crystal, namely $NaNbSe_2$, the d_{z^2} band would be complete, the result being a semiconductor akin to $MoSe_2$.

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

Cavendish Laboratory,
University of Cambridge,
Cambridge.

J. V. Acrivos†
W. Y. Liang
J. A. Wilson
A. D. Yoffe
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† Now at Department of Chemistry, San Jose State College, California, USA.