1-1-1971

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

Follow this and additional works at: https://scholarworks.sjsu.edu/chem_pub

Part of the [Physical Chemistry Commons](#)

Recommended Citation

Juana Vivó Acrivos, Y. Liang, J. Wilson, and A. Yoffe. "Optical Studies of Metal- Semiconductor Transmutations Produced by Intercalation" *Journal of Physics C: Solid State Physics* (1971): L18-L20.

This Article is brought to you for free and open access by the Chemistry at SJSU ScholarWorks. It has been accepted for inclusion in Faculty Publications, Chemistry by an authorized administrator of SJSU ScholarWorks. For more information, please contact scholarworks@sjsu.edu.

GARCÍA-MOLINER, F. and RUBIO, J., 1969, *J. Phys. C: Solid St. Phys.*, **2**, 1789–96.

MORSE, P. M. and FESHBACH, H., 1953, *Methods of Theoretical Physics*, (New York: McGraw-Hill).

Optical studies of metal-semiconductor transmutations produced by intercalation

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, Omluo and Jelinek 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 $<-78^\circ\text{C}$, 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 ($>1\mu\text{m}$), 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. Elec
(a), pure crysta
(c), same cryst
shifted to aid c
the band edge.

vapour is gradually
of the pure materia
If it is assumed t
electrons into the
in terms of the rigid

Figure 2. Elec
(a), pure crysta
coefficients are

† Cf. tungsten 'bro
Compounds, 1962 An

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* $\text{Na} \rightarrow \text{Na}^+ + e$, donating mobile electrons into the $X\text{--}M\text{--}X$ 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.

2, 1789–96.
(New York: McGraw-Hill).

Mutations

products of MoS_2 and NbSe_2
model.

metal dichalcogenides with
on with the superconduct-
compounds. Thus pyridine
sandwiches in niobium and
measurements it is concluded
the sheets (Gamble *et al.*
during vapour trans-
gap, and some of these
(Anzenhofer *et al.* 1970,

crystals of MoS_2 and NbSe_2
already a good deal of
(Mullinek 1970). The results
of the band model recently
son and Yoffe, 1969).

are fixed on the window of
sandwiches of these small
of solid ammonia was
ved by a film of metallic
f sodium atoms onto the
s it was possible to pro-
n spectrum was measured
e specimen. An absolute

given in figures 1 and 2.
figures 1 (b) and (c) are
(% of saturation limit) and
noted that the addition of
, D and those at higher
le a saturating concentra-
all the absorption peaks
long wavelength side of
(a)). On intercalation of
e main absorption edge,
ngths. Indeed the spectrum
o S_2 family – particularly
, p. 284). If air or water

itzer (1962).

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
26th October, 1970

- ACRIVOS, J. V., and PITZER, K. S., 1962, *J. Phys. Chem.* **66**, 1993.
ANZENHOFER, K., VAN DEN BERG, J. M., COSSEE, P., and HELLE, J. N., 1970, *J. Phys. Chem. Solids*, **31**, 1057.
GAMBLE, F. R., DI SALVO, F. J., KLEMM, R. A., and GEBALLE, J. H., 1970, *Science*, **168**, (3931) 568.
HULLIGER, F. and POBITSCHKA, E., 1970, *J. Solid St. Chem.*, **1**, 117.
OMLOO, W. P. F. A. M., and JELLINEK, F., 1970, *J. Less Comm. Metals*, **20**, 121.
RUDORFF, W., 1965, *Chimia*, **19**, 489.
VOORHOEVE, J. M. and ROBBINS, M., 1970, *J. Solid St. Chem.*, **1**, 134.
WILSON, J. A. and YOFFE, A. D., 1969, *Adv. Phys.*, **18**, 193.

† Now at Department of Chemistry, San Jose State College, California, USA.

Nuclear spin translation of

Abstract
the char
been stu
reveals
isotropic

Recently (Lenk
following depende
 ω_0 (low temperatu

The value of the e
while for the polyis

These results sho
stochastic rotation
density with $\alpha = 2$
Planck equation fo

Torrey (1953) an
equation for the ca
case, proposed by

$$J(\omega) = B\tau$$

with $u = (\omega_0\lambda)^{1/2}$.

This relation is s

The nuclear rela
to the law $\omega_0^{3/2}$. Th
found for the elasti
and experimental v
other than isotropi

On the other ha
swollen by 1 cc of
explained by the in
interproton distanc
probability of rota
exponent $\alpha = 2$. T
 $\alpha_{\text{rot}} = 2$.

Laboratoire de Sp
Faculté des Science
38 St Martin d'He

BLOEMBERGEN, N., 1
HUBBARD, P. S., 196