

X-RAY SPECTROSCOPIC STUDY OF CHEMICAL BONDING IN NiSe AND NiSe₂

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Received July 31, 1967

(Communicated by Dr. S. S. Joshi, F.A.Sc.)

ABSTRACT

The K absorption spectra of nickel and selenium have been recorded photographically in the pure metals and the compounds NiSe and NiSe₂. It has been observed that the Ni discontinuity shifts toward the high energy side with respect to that in the pure metal by about 5.0 eV for NiSe and about 6.7 eV for NiSe₂. The Se edge in both these compounds is found to shift by about 2.6 eV toward the low energy side with respect to that in pure selenium. From these results it is possible to obtain the bonding pictures for the compounds. The compound NiSe appears to have resonating p^3 type of bonding. For NiSe₂ the orbitals involved in the bonding are d^2sp^3 for the metal atom and sp^3 for the metalloid atom. The electrical behaviour of the compounds has been explained on the basis of these bonding pictures.

INTRODUCTION

In some earlier publications¹⁻³ X-ray spectroscopic studies of the intermetallic compounds CoSe, MnSe, MnSe₂ and CoSe₂ have been described. It has been shown how it is possible to interpret the X-ray spectroscopic data to obtain information on the chemical bonding in these compounds. In this paper, which is in continuation with the earlier ones, we report the results of our investigations on the K absorption spectra of nickel and selenium in two intermetallic compounds, nickel selenide (NiSe) and nickel diselenide (NiSe₂).

EXPERIMENTAL

The technique of recording the X-ray absorption discontinuities has been described in detail in the earlier publications. The Ni discontinuity

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was studied in the pure metal and in the compounds using a copper target Machlett X-ray tube as the source of radiation. The $K\beta_{1,3}$, $K\beta_{3,5}$ and $K\alpha_2$ lines of copper served as reference lines for the measurement of the Ni discontinuity. The compounds, which were prepared by suitably heating the constituent elements in vacuum-sealed silica tubes as described in the earlier publications, were controlled by the X-ray diffraction method.

RESULTS

The wavelengths and the corresponding energies of the Ni K and the Se K absorption edges in the pure metals and in the compounds NiSe and NiSe₂ are given in Tables I and II. Our wavelength for the nickel metal

TABLE I
Experimental data on the Ni K absorption discontinuity

Absorber	λ (X.U.)	ν/R	Energy (eV)	ΔE
Ni metal (Bearden)	1484.99	613.65
Ni metal (Authors)	1484.95 ± 0.06	613.67	8330.6 ± 0.4	..
NiSe	1484.05 ± 0.06	614.04	8335.6 ± 0.4	+5.0
NiSe ₂	1483.75 ± 0.06	614.17	8337.3 ± 0.4	+6.7

TABLE II
Experimental data on the Se K absorption discontinuity

Absorber	λ (X.U.)	ν/R	Energy (eV)	ΔE
Se pure	977.82 ± 0.07	931.94	12651.1 ± 0.5	..
NiSe	978.01 ± 0.07	931.76	12648.6 ± 0.5	-2.5
NiSe ₂	978.03 ± 0.07	931.74	12648.4 ± 0.5	-2.7

agrees very well with that given by Bearden,⁴ which is also included in Table I for the sake of comparison. It can be seen from Table I that the Ni absorption edge in both the compounds shifts toward the high energy side with respect to that in the pure metal; however, the shift is larger for NiSe₂ than for NiSe. On the other hand, the Se discontinuity is found to shift toward the low energy side with respect to that in pure selenium. This shift is of the same order in both the compounds.

DISCUSSION

1. Crystal Structure

According to Grønvold and Jacobsen⁵ the compound NiSe has the NiAs (B₈) type structure. In this structure the transition metal atoms occupy the octahedral holes in a close-packed hexagonal array of metalloid atoms and each metalloid atom is surrounded by six transition metal atoms in the form of a trigonal prism. This structure is shown in Fig. 1. The close packing is perfect when the axial ratio $c/a = 1.63$. In NiSe, however, $c/a = 1.46$, the value of a and c being 3.661 Å and 5.366 Å respectively.

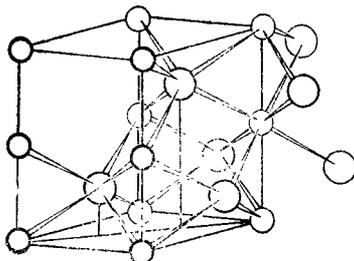


FIG. 1. Nickel arsenide [B₈] structure, smaller circles represent metal atoms larger circles represent metalloid atoms.

The compound NiSe₂ is found to crystallize in pyrite type structure, which has been described in detail in our previous paper.³ The lattice parameter a for this compound is found to be 5.960 Å.⁵

2. Chemical Bonding

(a) *NiSe*.—The outer electronic structure of the nickel atom is $3d^84s^2$ and that of selenium atom is $4s^24p^4$. According to Pearson⁶ in the compound NiSe it is the promotion and transfer of electrons into the empty $4p$ metal orbitals that gives rise to resonating p^3 bonds, as in the case of CoSe and MnSe. Suchet⁷ has given another bonding picture for this compound in which the bonding takes place due to d^2p orbitals for the metal atom

and the p^3 orbitals for the metalloid atom. Both these bonding pictures are compatible with the crystal structure of the compound. We shall now discuss our X-ray spectroscopic results in the light of the above two bonding pictures.

It has been shown in our earlier papers that the inflexion point on the absorption edge of a metal as well as in a semiconductor represents the top of the outermost-filled band. In the case of NiSe (and also NiSe₂) this must be so, since the compound shows metallic conductivity. Thus the observed shift of the Ni K edge in NiSe suggests a shift of the top of the valence band toward the high energy side, indicating the promotion of the metal $4s$ electrons into the $4p$ orbitals. The shift of the Se K edge in NiSe toward the low energy side suggests that a p electron of selenium is transferred into the nickel atom.

Our results confirm that the bonding in this compound takes place due to the promotion of the nickel electrons into the higher orbitals and due to the transfer of an electron from selenium into the metal atom. However, it is not possible from our results alone to rule out one of the two different bonding pictures given by Pearson and Suchet (see Fig. 2). The magnetic criterion can be useful here to choose the correct bonding picture.

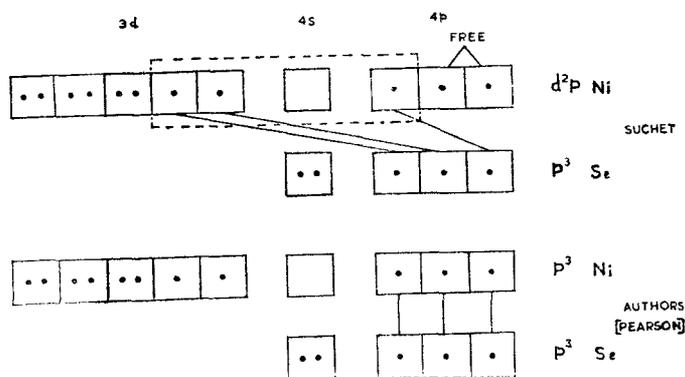


FIG. 2. Chemical bonding in NiSe.

According to Grønvd and Jacobsen⁵ NiSe is antiferromagnetic in nature. Suchet's bonding picture makes NiSe diamagnetic. On the other hand, Pearson's picture with two free spin d electrons makes the nickel ion paramagnetic. Since in this compound each metal atom is surrounded by two metal atoms rather closely ($d = 2.68 \text{ \AA}$) exchange interactions between

the paramagnetic ions lead to the observed antiferromagnetism. Hence, Pearson's bonding picture, which is compatible with structural, magnetic as well as X-ray spectroscopic data, seems to be more convincing than that given by Suchet.

(b) $NiSe_2$.—The observed shift of the Ni absorption edge in this compound indicates that some higher empty orbitals above the $3d$ and $4s$ ones are filled. The shift for $NiSe_2$ being larger than for $NiSe$, it can be assumed that the electrons are promoted even beyond the $4p$ orbitals in this compound. The shift of the Se K edge toward the low energy side provides evidence for the transfer of electrons from the selenium atoms into the nickel atom. It appears from these results that the bonding for the metal atom in this compound takes place due to d^2sp^3 hybridized orbitals of nickel, into which its s electrons and the four electrons borrowed from two selenium atoms are redistributed. For the selenium atoms the bonding then takes place due to hybridized sp^3 orbitals. In Fig. 3 is shown our bonding picture for $NiSe_2$ along with that given by Suchet. Had Suchet's picture been correct, the Ni K edge would have shifted toward the low energy side as against the shift to the high energy side observed by us.

Both the bonding pictures shown in Fig. 3 are compatible with the octahedral and tetrahedral co-ordinations of the Ni and Se atoms in the compound. However, our bonding picture gives essentially covalent character to the bonds, whereas in Suchet's picture the bond character is of the ionic-covalent type. The observed magnetic moment of the compound can be attributed to the two free $4d$ electrons.

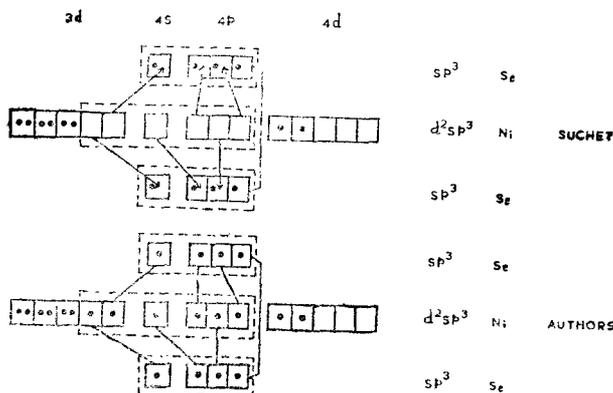


FIG. 3. Chemical bonding in $NiSe_2$.

3. *Electrical Behaviour*

Both NiSe and NiSe₂ are known to be metallic conductors.⁵ The metallic conductivity of NiSe can be explained as follows. In this compound the electrons in the 3*d* shell of nickel do not take part in chemical bonding and therefore one might at first sight expect them to lie in discrete states. However, as the axial ratio c/a ($= 1.46$) for this compound is appreciably smaller than the ideal ratio 1.63 for the NiAs type structure, the metal atoms along the *c*-axis approach each other rather closely. Owing to mutual overlap of the wave-functions of the *d* electrons a conduction band is formed which runs throughout the crystal lattice. Free motion of electrons in this band gives rise to metallic conductivity in this compound. The metallic conductivity of NiSe₂ can be attributed to the outermost 4*d* electrons which do not participate in bonding and hence remain free.

SUMMARY AND CONCLUSIONS

The X-ray spectroscopic study, in emission as well as absorption, of the selenides and diselenides of manganese, cobalt and nickel has been carried out using the bent crystal technique. It has been shown, probably for the first time, how it is possible to use such X-ray data for arriving at the correct bonding pictures, which determine the physical properties of the compounds.

The K absorption discontinuities of the constituent metals in the compounds MnSe, CoSe and NiSe were found to shift toward the high energy side in comparison to those of the respective metals. The MnKβ₅ emission band, which corresponds to the transition of the outermost manganese electrons into the K level, was found to shift in MnSe *en bloc* toward the high energy side. The Se absorption discontinuity in the above compounds, on the other hand, was found to shift toward the low energy side with respect to that in pure selenium.

The metal K absorption discontinuities in the compounds MnSe₂, CoSe₂ and NiSe₂ were also found to shift towards the high energy side, but the observed shift for them is higher than that in the selenides. The shift of the Mn Kβ₅ emission band in MnSe₂ is again found to be higher than that in MnSe. The Se K absorption discontinuity in these compounds is found to shift toward the low energy side, as in the selenides.

The shifts of the metal absorption edges indicate the filling of the normally empty higher orbitals in the compounds by promotion and transfer of electrons. Evidence for the transfer of electrons comes from the shifts

of the Se discontinuity in the compounds. It is the promotion and transfer of electrons which ultimately gives the bonding in the compounds. The bondings obtained in this work and those of Pearson and Suchet are given in Table III. The bond character, which plays an important role in determining the electrical behaviour of the compounds, is also shown in this table.

TABLE III

Compound	Chemical bonding					
	Pearson		Suchet		Authors	
	Metal atom	Metalloid atom	Metal atom	Metalloid atom	Metal atom	Metalloid atom
MnSe ..	$p^3\ddagger$	$p^3\ddagger$	$p^3\ddagger$	$p^3\ddagger$	$p^3\ddagger$	$p^3\ddagger$
CoSe ..	$p^3\ddagger$	$p^3\ddagger$	$d^2p\ddagger$	$p^3\ddagger$	$p^3\ddagger$	$p^3\ddagger$
NiSe ..	$p^3\ddagger$	$p^3\ddagger$	$d^2p\ddagger$	$p^3\ddagger$	$p^3\ddagger$	$p^3\ddagger$
MnSe ₂	sp^3d^2*	sp^3*	$sp^3d^2\ddagger$	$sp^3\ddagger$
CoSe ₂	d^2sp^3*	sp^3*	$d^2sp^3\ddagger$	$sp^3\ddagger$
NiSe ₂	d^2sp^3*	sp^3*	$d^2sp^3\ddagger$	$sp^3\ddagger$

Bond character: * Predominantly ionic; ‡ Predominantly covalent.

The semiconductivity of MnSe and MnSe₂ has been attributed to the predominantly directional covalent bondings in these compounds. The metallic conductivity of CoSe, NiSe, CoSe₂ and NiSe₂ has been attributed either to the crystal structure (in the case of CoSe and NiSe) or to the outermost free electrons (in the case of CoSe₂ and NiSe₂) which do not take part in bonding.

It would be interesting to extend this study to many other inter-metallic compounds. Such a study, preferably carried out with an instrument of higher resolving power and larger dispersion, would help in a better understanding of the physico-chemical forces in them. It is quite likely that it may eventually lead to the much sought for criterion of semi-conductivity in these compounds.

ACKNOWLEDGEMENT

The authors are thankful to the Directorate of Industries, Government of Maharashtra, Bombay, for financing a research scheme under which this work has been done.

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