

## X-ray spectroscopic study of zirconium and molybdenum diselenides

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**Abstract.** The K absorption spectra of zirconium, molybdenum and selenium in  $ZrSe_2$  and  $MoSe_2$  have been recorded photographically using a Cauchois type bent crystal (mica) spectrograph. The absorption edge shifts are used along with the data for  $NbSe_2$  (Bhide and Bahl 1971 *J. Phys. Chem. Solids* **32** 1001) to propose bond schemes for these compounds.

**Keywords.** X-ray spectroscopy; K absorption spectra; chemical bonding;  $ZrSe_2$ ;  $MoSe_2$ ;  $NbSe_2$ .

### 1. Introduction

The dichalcogenides of transition metals form a structurally and chemically well-defined family. The electrical behaviour of these compounds spans a wide spectrum, from an insulator like  $HfS_2$  (Conroy and Park 1968) to superconductors like  $TaS_2$  (Van Maaren and Schaeffer 1967). Attempts have been made to understand the behaviour of these materials through theoretical (Bromley *et al* 1972) as well as experimental investigations (Wilson and Yoffe 1969) of their band structure.

It is well known that the nature of the chemical bond in a solid provides an understanding of the physical behaviour of the material and that x-ray spectroscopy is a promising method for the study of the nature of chemical bonding in a solid. Amongst the diselenides of zirconium, niobium and molybdenum, the middle member  $NbSe_2$  has a metallic behaviour (Kershaw *et al* 1967) in contrast to the semiconducting nature of the end members,  $ZrSe_2$  and  $MoSe_2$  (Evans and Hazelwood 1971). With a view to understanding this irregular behaviour from the point of view of the chemical bond we undertook x-ray spectroscopic investigation of these compounds.

We report in this paper the K absorption spectra of the atoms in  $ZrSe_2$  and  $MoSe_2$  and compare these spectra with the spectrum of  $NbSe_2$  obtained by Bhide and Bahl (1971). We propose certain bond schemes for these compounds which explain their observed physical behaviour.

## 2. Experimental

A Cauchois type bent crystal (mica) spectrograph of diameter 400 mm was used to analyse the x-radiation transmitted through absorbers of the material under investigation. A Philips x-ray generator PW 1009 was used as the source of radiation. The experimental technique has been described earlier (Bhide *et al* 1971). The reference lines used and other conditions for recording the spectra are given in table 1. Six films were obtained for each absorption edge and were microphotometered with a magnification 50 ×. Each film was microphotometered at eight points. The position of the absorption edge was taken at the midpoint of the absorption jump on the microphotometer record. The spread in value indicated with each wavelength of the absorption edge is the mean deviation of at least forty measurements.

## 3. Results

The wavelengths of K absorption edges for zirconium, niobium and molybdenum in the respective metals and in the compounds are given in table 2. The observed values of the wavelengths for the metals are in good agreement with those reported by Ross (1933). The wavelengths of the K edge for selenium in elemental selenium

Table 1. Reference lines used and conditions under which the spectra were recorded

Absorption edge	Wave-length xu	Order	Reference line	Wave-length xu	Order	Tube target	Tube operation	Exposure time hr
Selenium K	977·8	2nd	Mo K <sub>α<sub>1</sub></sub>	712·105	3rd	Mo	20 kV	8 10
			Mo K <sub>β<sub>13</sub></sub>	630·978	3rd		15 mA	
Zirconium K	687·4	2nd	Mo K <sub>α<sub>1</sub></sub>	712·105	2nd	Mo	30 kV	8 10
			Mo K <sub>β<sub>13</sub></sub>	630·978	2nd		10 mA	
Molybdenum K	618·4	2nd	WL <sub>β<sub>1</sub></sub>	1279·19	1st	Cu	35 kV	8 10
			WL <sub>r<sub>1</sub></sub>	1096·30	1st		10 mA	

Table 2. Data on the K absorption edges of zirconium, niobium and molybdenum in their diselenides

Absorption edge	Substance	Wavelength xu	Energy E, eV	Shift ΔE, eV
Zirconium K	Zr metal	687·43 ± 0·04	17997·25	+2·89
	ZrSe <sub>2</sub>	687·32 ± 0·04	18000·64	
Molybdenum K	Mo metal	618·55 ± 0·05	20002·28	-4·87
	MoSe <sub>2</sub>	618·69 ± 0·05	19997·41	
Niobium K	Nb metal	651·69 ± 0·02	18984·70	-2·43
	NbSe <sub>2</sub>	651·76 ± 0·03	18982·27	

Table 3. Data on selenium K absorption edge in the diselenides of zirconium, molybdenum and niobium

Selenium K edge in	Wavelength $\lambda$ , $\mu$	Energy $E$ , eV	Shift $\Delta E$ , eV
Selenium	$977.79 \pm 0.04$	12653.22	
ZrSe <sub>2</sub>	$977.90 \pm 0.04$	12651.89	-1.42
MoSe <sub>2</sub>	$977.85 \pm 0.04$	12652.45	-0.77
NbSe <sub>2</sub>	$978.01 \pm 0.05$	12650.38	-2.07

and in its compounds are listed in table 3. The zirconium K edge in ZrSe<sub>2</sub> is found to shift to higher energy as compared to that in the metal, while the niobium K edge in NbSe<sub>2</sub> and the molybdenum K edge in MoSe<sub>2</sub> are shifted to lower energy. The selenium K edge in all the three compounds is shifted to lower energy.

#### 4. Discussion

Zirconium, niobium and molybdenum belong to the early part of the second transition series and have electronic configurations (Kr) 4d<sup>2</sup>5s<sup>2</sup>, (Kr) 4d<sup>4</sup>5s<sup>1</sup> and (Kr) 4d<sup>5</sup>5s<sup>1</sup> respectively. The valence bands in these metals are therefore expected to be built up from the 4d and 5s states with a considerable admixture of 5p states (Altmann and Bradley 1967, Morin 1961). In the band structure of selenium [electronic configuration (A) 4s<sup>2</sup>4p<sup>4</sup>], the valence band is constituted from the 4s and two of the three p states and is separated from the conduction band formed from the remaining p states (Reitz 1957). When the transition metals combine with selenium to form the diselenides, the changes occurring in the valence bands of these metals would therefore be reflected in the K absorption (1s → p states in the band) spectra of the atoms in these compounds.

Selenium K absorption edge in the diselenides lies at a lower energy as compared to that in elemental selenium (table 3), the shift in MoSe<sub>2</sub> being less than that in ZrSe<sub>2</sub> and NbSe<sub>2</sub>, in agreement with the observation (Agrawal and Verma 1970, Sapre 1972) that for the same valence state of an atom, the shift is smaller, larger the covalency in the compound. The covalency of the compounds on the Pauling scale is about 65% for ZrSe<sub>2</sub>, 75% for NbSe<sub>2</sub> and 92% for MoSe<sub>2</sub>. Contrary to the above rule, the shift for NbSe<sub>2</sub> with a larger covalency is more than that in ZrSe<sub>2</sub>. This deviation could therefore be due to some other reason such as a change in the nature of hybridization. The shift of the K edge to lower energy in all the three compounds indicates a depletion of the valence band of selenium in the process of compound formation, due to donation of electrons to the cation.

In ZrSe<sub>2</sub>, zirconium K edge shifts to higher energy as compared to that in the metal (table 2). The high energy side shift indicates a greater filling of the zirconium outer orbitals, either due to promotion of inner electrons or acceptance of electrons from the anion. The donation of electrons by selenium is indicated by the lower energy side shift of the selenium K edge in the compound.



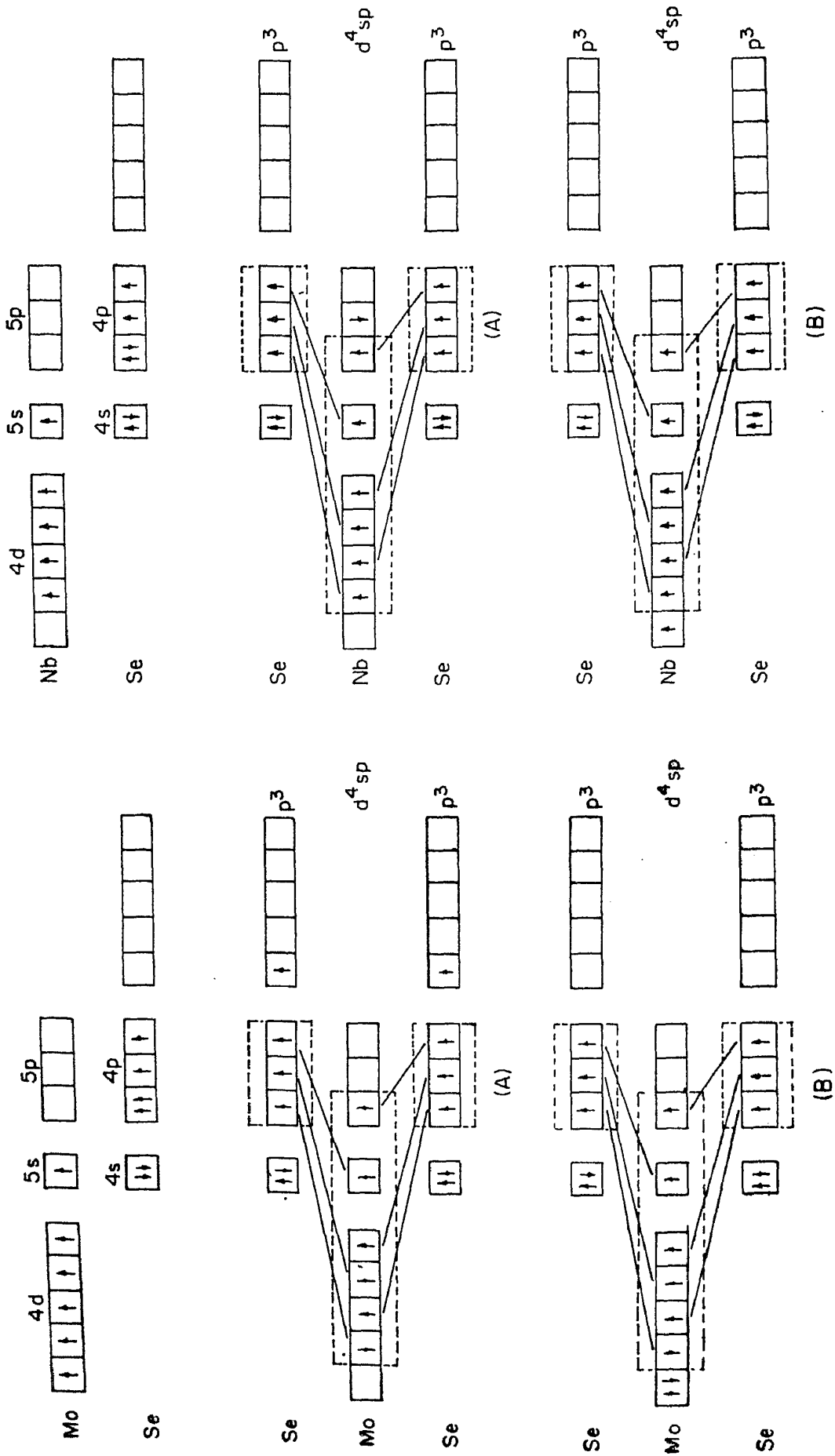
Figure 1. Bond scheme for  $ZrSe_2$ .

The layered structure of  $ZrSe_2$  (Greenaway and Nitsche 1968) endows each zirconium atom with an octahedral coordination of six selenium atoms. The formation of six hybrid  $d^2sp^3$  orbitals on zirconium would provide the necessary six bonds. On the other hand each selenium atom is bonded to its three zirconium neighbours by means of three hybrid  $p^3$  bonds. A zirconium atom has four valence electrons of its own and acceptance of two electrons from the two selenium atoms (one from each) would enable it to form six bonds with its neighbours. Each selenium atom donating one of its four p electrons has three electrons left, with which it forms bonds with its three zirconium neighbours. Thus a fully saturated bonding with two electrons per bond as shown in figure 1 could be built up.

The above bonding picture is in agreement with the x-ray spectroscopic data. The redistribution of the four valence and the two accepted electrons in the six  $d^2sp^3$  orbitals on zirconium would lead to a greater filling of the p orbitals and thus shift the K edge to a higher energy. The donation of a p electron by selenium would lead to a depletion of its p orbitals and cause a shift of the K edge to a lower energy, as observed by us.

Thus our x-ray spectroscopic data together with the structural information lead to an ionocovalent bond between zirconium and selenium ions in  $ZrSe_2$ . Comparison of the ionic bond length (2.72 Å) with the observed bond length (2.66 Å) indicates an appreciable ionic contribution to the bond (estimated at 30% on Pauling scale). A compound with an ionocovalent bond with an appreciable ionic contribution is likely to be a semiconductor (Mooser and Pearson 1956), as indeed  $ZrSe_2$  is with a band gap of 1.2 eV (Lee *et al* 1969). The bonding scheme (figure 1) is also in agreement with the diamagnetic nature of the compound.

A molybdenum ion in  $MoSe_2$  has six selenium neighbours in a trigonal prismatic co-ordination (James and Levik 1963). On the consideration of bond angles in such a coordination Hultgren (1932) postulated a  $d^4sp$  hybridization of the orbitals on the central ion. A molybdenum atom with its six valence electrons ( $d^5s^1$ ) is in a position to provide six electrons for the six hybrid  $d^4sp$  bonds. This would

Figure 2. Bond schemes for  $\text{MoSe}_2$ Figure 3. Bond schemes for  $\text{NbSe}_2$

necessitate promotion of an inner d electron to the outer p orbitals. Selenium atoms in their turn would form three  $p^3$  bonds with their molybdenum neighbours, the extra p electron being promoted to the outer d orbitals. The bonding scheme for  $MoSe_2$  would then be as shown in figure 2A.

Assuming that the above picture is valid, the promotion of an inner d electron to outer p orbitals would cause a partial filling of the band, tending to shift molybdenum K absorption edge in  $MoSe_2$  to a higher energy. Similarly, the filling of the outer orbitals on selenium due to electron promotion would cause the selenium absorption edge also to move to a higher energy. The observed shifts of molybdenum and selenium K edges in  $MoSe_2$  as compared to those in the respective metals are just in the opposite direction to that indicated on the basis of the above bond scheme.

The bonding scheme shown in figure 2A is not only at variance with the x-ray spectroscopic data but also with the electrical properties of the compound. In the bonding scheme each selenium atom is left with one electron in the outermost orbitals. This electron has no role in the bonding of the compound, and therefore is free and should lead to a metallic behaviour of the compound; but in fact  $MoSe_2$  is known to be a semiconductor (Lele *et al* 1967).

The shift of the selenium K edge in  $MoSe_2$  to a lower energy indicates, as in  $ZrSe_2$ , a donation of a p electron by selenium to molybdenum, so that the selenium ion is left with three electrons with which to form bonds with its three molybdenum neighbours. Molybdenum ion thus has eight electrons, six of its own and two accepted from selenium. The distribution of these electrons amongst its orbitals poses a difficulty which can be overcome by pairing two electrons in a d orbital and distributing the remaining six amongst its six  $d^4sp$  orbitals. The bond scheme envisaged is as shown in figure 2B.

This scheme (figure 2B) leads to a shift of the selenium edge to a lower energy as discussed in the previous paragraph. Figure 4 shows microphotometer traces of the molybdenum K edge in molybdenum metal and  $MoSe_2$ . Each edge is

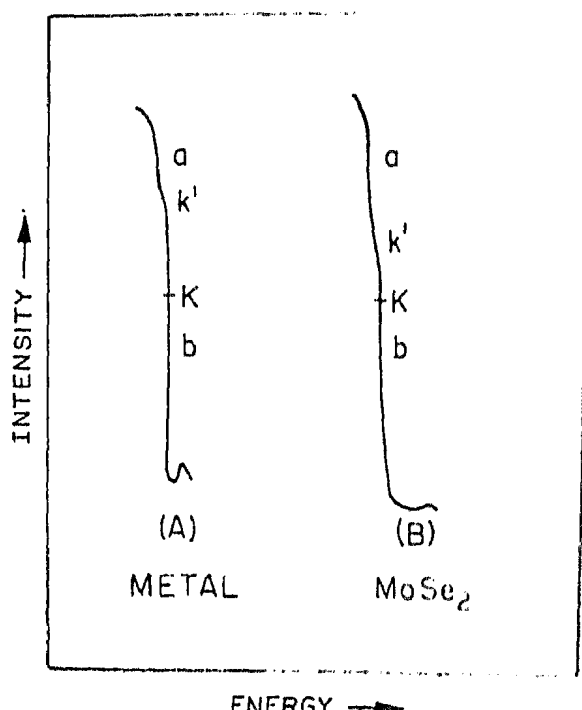


Figure 4. Microphotometer traces of molybdenum K edge in Mo metal and  $MoSe_2$ .

found to be made up of two parts, a region of initial absorption denoted by 'a' and a region of final absorption denoted by 'b' the two regions being separated by a shoulder K'. The initial absorption may be due to an electron transition to the 4d — 5s band with an admixture of p states while the final absorption is due to an electron transition to the 5p states in the band. The observed decrease in the separation of 'a' and 'b' in going from the metal to the selenide indicates a lowering of the p states in relation to the d states due to a greater mixing on account of hybridization. The band as a whole would contract due to its greater degree of filling. The molybdenum edge in that case would move to a lower energy as observed by us.

The x-ray spectroscopic studies of MoSe<sub>2</sub> thus support the bonding scheme given in figure 2B which provides an ionocovalent bonding between molybdenum and selenium ions. Absence of unpaired electrons on molybdenum indicates a diamagnetic behaviour of the compound, as indeed reported by Wilson and Yoffe (1969).

The coordination characteristics in NbSe<sub>2</sub> (Brown and Beerstein 1965) are identical with those of MoSe<sub>2</sub>. The niobium K absorption edge as well as selenium K edge shift to lower energy in NbSe<sub>2</sub> as compared to those in the respective metals, similar to that observed in MoSe<sub>2</sub>. The similarity of the structural aspects as well as x-ray absorption data suggest a similar type of bond formation as in MoSe<sub>2</sub>. Thus each selenium atom donates an electron to the niobium atom. The seven electrons which a niobium ion now possesses (five original and two accepted from selenium) can get distributed in seven orbitals. The six d<sup>4</sup>sp hybrid orbitals of niobium required for bonding to its six selenium neighbours accommodate six of the seven electrons, while the assignment of an orbital to the remaining electron is uncertain. If this electron is assigned to a p orbital, there is a greater filling of the p orbitals (figure 3A). Such a filling of the p orbitals should cause the K edge of niobium in NbSe<sub>2</sub> to move to a higher energy. The observed shift of the edge to a lower energy, therefore, does not favour this assignment of the electron to a p orbital. If the additional electron is placed in the d orbital remaining vacant after the formation of a d<sup>4</sup>sp hybrid, resulting in a greater filling of the d band, the K edge for niobium in NbSe<sub>2</sub> would shift to a lower energy as in MoSe<sub>2</sub>. The smaller shift of the edge in NbSe<sub>2</sub> could be due to a lesser degree of filling of d orbitals as compared to that in MoSe<sub>2</sub>. The bond scheme for NbSe<sub>2</sub> is shown in figure 3B.

An interesting aspect of the bonding scheme for NbSe<sub>2</sub> is the behaviour of the unpaired electron in the d orbitals of niobium ion. *Prima facie*, presence of an unpaired electron on the niobium ion should lead to a paramagnetic behaviour in NbSe<sub>2</sub>. In a predominantly ionic compound, the electron would be localized on the niobium ion causing paramagnetic behaviour. But in a predominantly covalent compound like NbSe<sub>2</sub> the electron cannot remain localized on the ion but is partly delocalized. This, therefore, leads to metallic behaviour of the compound. The contribution of the electron to the magnetic behaviour should be that of a conduction electron, *i.e.*, it should lead to Pauli paramagnetism in the compound. In MoSe<sub>2</sub>, the two electrons in the non-bonding d orbital are more localized due to the stabilizing effect of the pairing energy. The difference between

the behaviour of  $MoSe_2$  and  $NbSe_2$  is essentially due to the different behaviour of the electrons occupying the non-bonding d orbital. While  $MoSe_2$  is a diamagnetic semiconductor,  $NbSe_2$  has metallic behaviour and exhibits Pauli paramagnetism tending towards band antiferromagnetism (Selte and Kjekshus 1965).

## 5. Conclusions

The x-ray spectroscopic data on  $ZrSe_2$ ,  $NbSe_2$  and  $MoSe_2$  are useful for the assignment of bond schemes for these compounds. Semiconductivity of  $ZrSe_2$  and  $MoSe_2$  appears to be associated with the participation of all the valence electrons in the bonding, each bond being fully saturated, thus strengthening the hypothesis of Mooser and Pearson (1956). The bond schemes provide a qualitative understanding of the electrical and magnetic behaviour of these compounds.

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