

# X-RAY SPECTROSCOPIC STUDY OF CHEMICAL BONDING IN MnSe<sub>2</sub> and CoSe<sub>2</sub>

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## ABSTRACT

X-ray absorption study of two intermetallic compounds MnSe<sub>2</sub> and CoSe<sub>2</sub> has been carried out using a Cauchois type bent crystal spectrograph. The metal K absorption edges in both the compounds are found to shift toward the high energy side with respect to the discontinuities in the pure metals. On the other hand, the Se K absorption edge in both these compounds is found to shift toward the lower energies. Emission study of the compound MnSe<sub>2</sub> has shown that the Mn Kβ<sub>5</sub> band in this compound is shifted toward the high energy side with respect to that in the pure metal. From the magnetic data and the results obtained in this work it is possible to obtain the chemical bonding pictures in these compounds. For MnSe<sub>2</sub> the bondings  $sp^3d^2$  for the metal atom and  $sp^3$  for the metalloid atom have been suggested. For CoSe<sub>2</sub> the bondings appear to be  $d^2sp^3$  for the metal atom and  $sp^3$  for the metalloid atom. These bondings are compatible with the pyrite type structure of these compounds. It is possible to explain the electrical behaviour of the compounds on the basis of these bonding pictures.

## INTRODUCTION

THE study of chemical bonding in intermetallic compounds<sup>1,2</sup> has attracted much attention in recent years, because it helps in explaining their electrical and magnetic properties. In earlier publications it has been shown by the present authors<sup>3,4</sup> that it is possible to utilise fruitfully X-ray spectroscopic data to bring information on chemical bonding in two simple intermetallic compounds cobalt selenide (CoSe) and manganese selenide (MnSe). In these particular cases only one type of bonding is possible theoretically, which has been confirmed by our work. However, there are some intermetallic compounds for which several types of bonding pictures may be

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visualised. It was therefore thought worthwhile to extend the X-ray spectroscopic method to some such compounds in order to see if this technique could be utilised to arrive at correct bonding pictures which would not only be compatible with the crystal structure of the compounds but would also explain their electrical and magnetic behaviour. The compounds MnSe<sub>2</sub> and CoSe<sub>2</sub> appeared particularly interesting, because although they have similar crystal structure their electrical properties are entirely different.

## EXPERIMENTAL

### 1. *Preparation of Compounds*

The method of preparing these compounds was more or less similar to that described in our previous paper.<sup>4</sup> The homogeneity and the crystal structure of the compounds were checked by taking their X-ray diffraction patterns. In the case of CoSe<sub>2</sub> the interplaner distances  $d$  were compared with those given in the ASTM tables. But since diffraction data was not available for MnSe<sub>2</sub> in the ASTM tables, the observed  $d$  values were compared with those calculated from the knowledge of the crystal structure of the compound (pyrite type,  $a = 6.170 \text{ \AA}$ ).<sup>5</sup> The agreements being very good it was concluded that the compounds were formed in stoichiometric proportion.

### 2. *X-ray Spectroscopic Technique*

The K absorption edges of Mn, Co and Se in the pure metals as well as in the intermetallic compounds were recorded on a 40 cm. Cauchois type bent crystal X-ray spectrograph, designed and fabricated in the Poona University Central Workshop. A photograph of the general experimental set-up is shown in Fig. 1. While the W L lines were used as reference lines for the measurements of the Co and Se discontinuities, the Fe K $\alpha_{1,2}$  lines were used for the measurement of the Mn edge. Emission study of the Mn K $\beta_5$  band in the compound MnSe<sub>2</sub> was carried out using a continuously evacuated hot cathode Beaudouin demountable X-ray tube. Details of the experimental technique can be found in our earlier publication.<sup>4</sup>

## RESULTS

The results of the measurements on the absorption discontinuities obtained in this work are given in Tables I and II for MnSe<sub>2</sub> and CoSe<sub>2</sub> respectively. It is found that the metal absorption edges in both the compounds shift towards the high energy side with respect to the discontinuities

in the pure metals. On the other hand, the Se K absorption discontinuity in both these compounds is found to shift towards the low energy side with respect to the discontinuity in pure selenium.

TABLE I  
*Experimental data on the K absorption discontinuities*

Absorber	$\lambda$ X.U.	$\nu/R$	Energy (E) eV	$\Delta E$ eV
<i>Manganese—</i>				
Mn Metal ..	1891.29 $\pm 0.06$	481.82	6540.8 $\pm 0.4$	..
MnSe <sub>2</sub> ..	1889.30 $\pm 0.06$	482.33	6547.7 $\pm 0.4$	+6.9
<i>Selenium—</i>				
Se pure ..	977.82 $\pm 0.07$	931.94	12651.1 $\pm 0.5$	..
MnSe <sub>2</sub> ..	978.09 $\pm 0.07$	931.69	12647.6 $\pm 0.5$	-3.5

TABLE II  
*Experimental data on the K absorption discontinuities*

Absorber	$\lambda$ X.U.	$\nu/R$	Energy (E) eV	$\Delta E$ eV
<i>Cobalt—</i>				
Co Metal ..	1604.84 $\pm 0.05$	567.83	7708.2 $\pm 0.3$	..
CoSe <sub>2</sub> ..	1603.37 $\pm 0.05$	568.35	7715.3 $\pm 0.3$	+7.1
<i>Selenium—</i>				
Se pure ..	977.82 $\pm 0.07$	931.94	12651.1 $\pm 0.5$	..
CoSe <sub>2</sub> ..	978.02 $\pm 0.07$	931.75	12648.4 $\pm 0.5$	-2.7

The results on the  $Mn K\beta_5$  band for the pure metal and for the compound  $MnSe_2$  are given in Tables III and IV for measurements at the maximum intensity and at the emission edge respectively. The band is found to shift in the compound *en bloc* towards the high energy side with respect to that in the pure metal. It also appears, as in the case of  $MnSe$  to be somewhat broadened and diffused.

TABLE III

*Experimental data on the  $Mn K\beta_5$  band (at the maximum intensity)*

	$\lambda$ X.U.	$\nu/R$	Energy (E) eV	$\Delta E$ eV
Mn metal ..	1892.01 $\pm 0.06$	481.64	6538.3 $\pm 0.4$	..
$MnSe_2$ ..	1890.24 $\pm 0.06$	482.10	6544.4 $\pm 0.4$	+6.1

TABLE IV

*Experimental data on the  $Mn K\beta_5$  band (at the emission edge)*

	$\lambda$ X.U.	$\nu/R$	Energy (E) eV	$\Delta E$ eV
Mn Metal ..	1891.31 $\pm 0.06$	481.82	6540.7 $\pm 0.4$	..
$MnSe_2$ ..	1889.40 $\pm 0.06$	482.31	6547.3 $\pm 0.4$	+6.6

## DISCUSSION

## 1. Crystal Structure

Several workers<sup>5-9</sup> have studied the crystal structure of the  $TX_2$  (Here T stands for the transition metal atom and X for the metalloid atom) type compounds. They are generally found to crystallize in pyrite ( $C_2$  type) structure which is shown in Fig. 2. In this structure, which is essentially cubic, each metal atom has six metalloid neighbours occupying the corners of an octahedron, whereas each metalloid atom has four tetrahedral neighbours. Among these neighbours one is another metalloid atom and the

remaining three are metal atoms, as shown in Fig. 2. According to Elliot<sup>5</sup> the compound  $MnSe_2$  has the pyrite structure with  $a = 6.170$  Å. Bøhm *et al.*<sup>6</sup> have shown that the compound  $CoSe_2$  has a similar structure with  $a = 5.854$  Å.

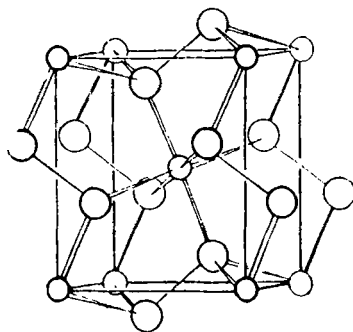


FIG. 2. Pyrite [ $C_2$ ] structure, smaller circles represent metal atoms, larger circles represent metalloid atoms.

## 2. Magnetic Properties

It is well known that the magnetic study provides valuable information regarding the number of unpaired  $d$  electrons in the transition metal atoms in compounds. Hence this study helps in distinguishing between the orbitals taking part in the chemical bonding and those not taking part in it.

Hastings *et al.*<sup>10</sup> have shown the compound  $MnSe_2$  to be antiferromagnetic in nature with effective magnetic moment 5.92 B.M. According to Hulliger and Mooser<sup>11</sup> this compound is associated with 'high spin' distribution of the  $d$  electrons and has five free spins. Bøhm *et al.*, who have studied the magnetic properties of  $CoSe_2$  ( $\mu_{eff} = 2.0$  B.M.), have shown that there is only one free spin  $d$  electron in the compound.

## 3. Chemical Bonding

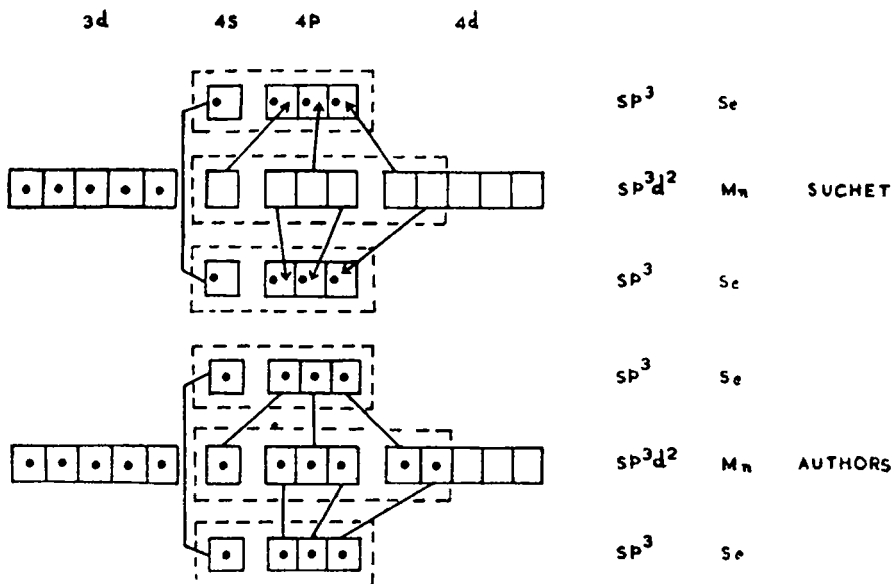
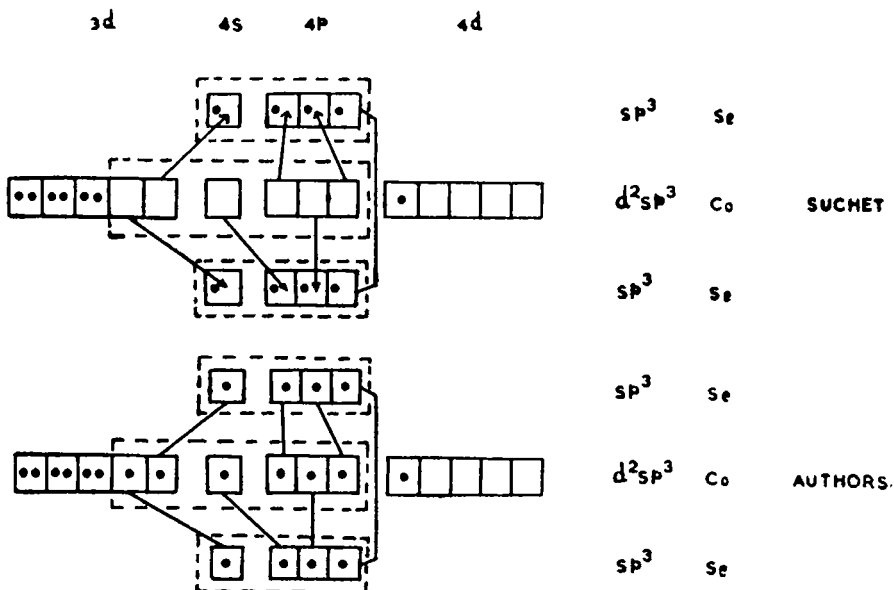
We shall now attempt to obtain the bonding pictures in these compounds with the help of our X-ray spectroscopic results. In this attempt we shall make use of the magnetic studies described earlier.

(a)  $MnSe_2$ .—Richtmyer *et al.*<sup>12</sup> have shown that the inflexion point on the absorption discontinuity of a metal represents the top of the outermost filled band. To interpret our X-ray spectroscopic results we make an analogous assumption that the inflexion point on the discontinuity of a semi-conductor represents the top of the valence band. Support for this

assumption comes from the K emission and absorption curves of selenium reported by Deslattes and deBen,<sup>13</sup> which show that the midpoint of the emission edge coincides with the inflexion point of the absorption discontinuity. The results obtained in this work on MnSe<sub>2</sub> which is a semiconductor<sup>11</sup> also corroborates this view. It can be seen from Tables I and IV that the energies of the Mn K $\beta_5$  emission edge and the corresponding absorption discontinuity in MnSe<sub>2</sub> are more or less the same. The observed shift of the Mn absorption edge and the emission band as a whole in this compound indicates that the top of the filled band has been shifted toward the high energy side. This means that some of the empty Mn orbitals lying above the 3*d* and 4*s* states which were not filled in pure manganese are filled in MnSe<sub>2</sub>. The shift of the Se absorption discontinuity toward the low energy side suggests that some electrons from the selenium atoms are transferred into the manganese atom in the compound. It can be safely assumed that these transferred electrons are one from the 4*s* and one from the 4*p* orbitals, which would give hybridized *sp*<sup>3</sup> bonding for the selenium atoms in the compound. This bonding is compatible with the tetrahedral surrounding of the selenium atoms.

From the magnetic study it is clear that all the five 3*d* electrons of manganese being free in the compound, they do not participate in chemical bonding. The bonding for the metal atom must then be due to the 4*sp*<sup>3</sup>*d*<sup>2</sup> hybridized orbitals, which get filled with the promoted two 4*s* manganese electrons and the four electrons borrowed from the two selenium atoms. This bonding is again compatible with the octahedral co-ordination of the metal atoms in the compound.

According to Suchet<sup>14</sup> also, the bonding in this compound is due to hybridized *sp*<sup>3</sup>*d*<sup>2</sup> orbitals for the metal atom and *sp*<sup>3</sup> orbitals for the metalloid atom. In Fig. 3 we have shown our bonding picture for the compound along with that given by Suchet. It must be emphasized here that our picture gives essentially covalent character to the bonding, whereas in Suchet's picture although the same orbitals are employed the bonding is of the ionic-covalent type. If Suchet's picture had been correct, then the Mn K absorption edge and also the Mn K $\beta_5$  band in the compound would have shifted toward the low energy side. It is interesting to mention here that according to Elliot,<sup>5</sup> who has made a detailed X-ray diffraction study of MnSe<sub>2</sub>, the bonds in this compound need not be of extreme ionic type.

FIG. 3. Chemical bonding in  $MnSe_2$ .FIG. 4. Chemical bonding in  $CoSe_2$ .

(b)  $CoSe_2$ —The X-ray spectroscopic results in the case of this compound are more or less similar to those for  $MnSe_2$ . It can be supposed

that in this compound also the outermost  $4p$  and  $4d$  orbitals of the metal atom get filled (as the Co K absorption discontinuity shifts towards higher energies) due to internal promotion as well as transfer of electrons from the selenium atoms. Here again evidence for this transfer of electrons comes from the shift of the selenium K discontinuity towards lower energies.

Our results seem to indicate that the bonding in this compound takes place due to  $d^2sp^3$  hybridized orbitals for the Co atom and due to  $sp^3$  orbitals for the selenium atoms. In Fig. 4 is shown this bonding picture along with that given by Suchet.<sup>14</sup> As in the case of  $MnSe_2$  in this compound also our picture gives a predominantly covalent character to the bonding as against the ionic character expected from Suchet's picture. In this case also if Suchet's picture had been correct the Co K edge in the compound would have shifted to the low energy side with respect to the edge in the pure metal. The observed magnetic moment of this compound can be attributed to the free  $4d$  electron.

#### 4. *Electrical Behaviour*

It is possible to explain the electrical behaviour of these compounds in the light of our bonding pictures.  $MnSe_2$  is known to be a semi-conductor<sup>11</sup> while  $CoSe_2$  has been found to be a metallic conductor.<sup>6</sup> Suchet's pictures suggesting predominantly ionic character in the chemical bonding fail to explain the observed electrical properties of these compounds, as it is well known that ionic compounds are generally insulators.

The chemical bonding with predominantly covalent nature as suggested by us is in accord with the observed semi-conductivity of  $MnSe_2$ . The metallic conductivity of  $CoSe_2$  can be attributed to the outermost  $4d$  electron which does not participate in bonding and hence remains free.

#### ACKNOWLEDGEMENT

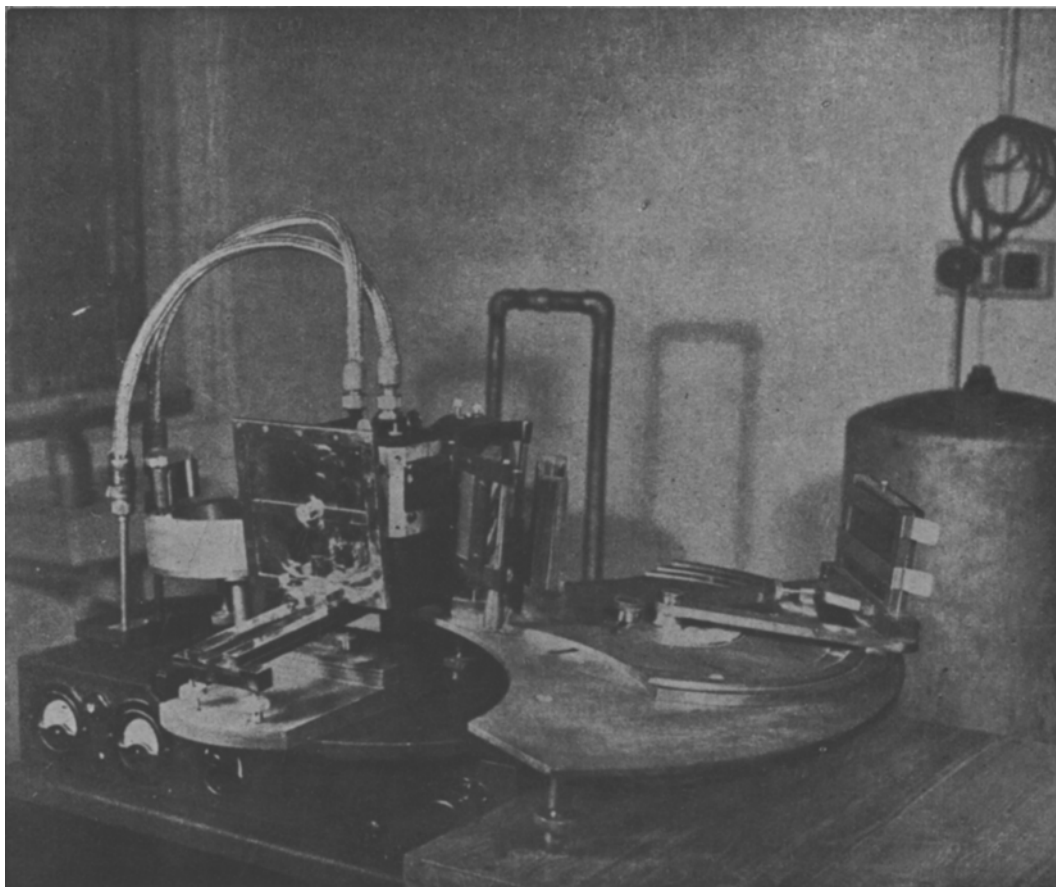
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**FIG. 1**