

X-RAY SPECTROSCOPIC EVIDENCE FOR CHEMICAL BONDING IN MANGANESE SELENIDE (MnSe)

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ABSTRACT

K absorption spectra of manganese and selenium have been recorded photographically in the pure metals and in the intermetallic compound manganese selenide (MnSe), employing a bent crystal X-ray spectrograph. It has been observed that the Mn K absorption discontinuity in MnSe shifts by 5.6 eV toward the high energy side with respect to the discontinuity in the pure metal. On the other hand, the Se K edge in MnSe is found to shift by 3.4 eV toward the low energy side with respect to the discontinuity in pure selenium. Also, emission work has revealed that the Mn $K_{\beta 5}$ band in the compound shifts by about 5 eV toward the high energy side with respect to that in the pure metal. It has been shown that these results confirm the resonating p^3 type of chemical bonding in the compound, as suggested theoretically by Pearson.

INTRODUCTION

In recent years the study of intermetallic compounds, particularly those of the transition metals, has attracted much attention, since some of these compounds have interesting semiconducting properties. Pearson^{1, 2} and Suchet³ have discussed theoretically the nature of chemical bonding in these compounds, which determines their electrical behaviour. However, not much experimental evidence seems to have been brought forth to confirm or assign them the appropriate chemical bondings.

As is well known X-ray spectroscopy provides a powerful and direct method of studying the distribution of outer electrons and the empty orbitals in solids.^{4, 5} Hence, this method can be applied to investigate the nature of chemical bonding in the intermetallic compounds. With this view we have studied the K absorption spectra of manganese and selenium in the pure forms and in a typical intermetallic compound MnSe. The manganese $K_{\beta 5}$

emission band, which corresponds to the transition of the outermost electrons into the K level, has also been studied for the pure metal and for the compound. The results of these studies have been discussed in the light of Pearson's theory of chemical bonding.

EXPERIMENTAL

(1) *Preparation of Manganese Selenide*

A.R. grade manganese and selenium powders were mixed in stoichiometric proportions and the mixture was vacuum-sealed in a silica tube. The sealed sample was slowly heated to 300° C. and was kept at this temperature for more than an hour, after which the temperature was gradually raised to 1200° C. in a period of three and half hours, this temperature then being maintained for five hours. The sample was afterwards allowed to attain the room temperature slowly in 18 hours. The compound formed was finely powdered by grinding. A control of the homogeneity and the crystal structure of the compound was done by studying its X-ray diffraction pattern, using a 114.6 mm. diameter Debye-Scherrer camera. The d values obtained for different planes of the compound being in complete agreement with those given in ASTM tables for MnSe, it was concluded that the compound formed was in stoichiometric proportion.

(2) *X-ray Spectroscopic Technique*

(a) *Absorption spectroscopy*—A sealed X-ray tube with tungsten target was employed to give a source of white radiation for recording the Se K absorption discontinuity. For studying the Mn K absorption discontinuity a sealed copper target tube was employed. The tubes were operated at 20 KV and 10 mA. A Cauchois type bent crystal X-ray spectrograph of diameter 40 cm., designed and constructed in the Poona University Central Workshop, was used for photographing the spectra. A mica crystal, used in a number of earlier investigations and hence with known crystal optics, was used as analyser. The (100) and ($\bar{2}01$) planes of mica were chosen as reflecting planes. Absorbing screens of the pure metals and of manganese selenide were made by spreading their fine powders on cellophane adhesive tape. The thicknesses of the screens varied from about 10 to 15 mgm./cm.² The spectra were photographed on Agfa ultraviolet plates, the exposure times varying between 15 and 20 hours. Microphotometer records of the spectra were obtained with magnification 50 on a Moll microphotometer. The wavelengths of the absorption discontinuities were measured at the inflexion point of the curves, according to the usual practice. The W L lines were

used as reference lines for the measurement of the Se discontinuity. In the case of the Mn discontinuity, the Fe K_{α_1, α_2} lines were used for reference.

(b) *Emission spectroscopy*—For the emission work a continuously evacuated hot cathode Beaudouin demountable X-ray tube was used. The Mn K emission spectra for the pure metal and for MnSe were obtained by spreading the sample mixed with an adhesive fluid over the anticathode of the tube, which was operated at 20 KV and 5 mA. The spectra, in this case, were photographed on a 20 cm. diameter Cauchois type bent crystal (mica) spectrograph, also fabricated in the Central Workshop of the Poona University. This smaller spectrograph, although poorer in dispersion as compared to the 40 cm. one, has a much higher luminosity and is therefore more suitable for registering the faint emission lines, such as the K_{β_5} band. The reference lines used for the measurement of this band were the K_{α_2} and K_{β_1} lines of manganese, which it is assumed are not appreciably affected by chemical combination.

RESULTS

In Fig. 1 are reproduced the Mn K absorption discontinuities for the pure metal and for MnSe taken over one another on the same photographic plate. The results of the measurements on the discontinuities obtained in this work are given in Table I, along with those for the pure metals given in Bearden's recent tables⁶ for comparison. It is found that the Mn K absorption edge in the compound shifts towards higher energies by about 5.6 eV, with respect to the discontinuity in the pure metal. The shift of the Mn K absorption edge towards higher energies can also be seen in Fig. 1. The Se K absorption edge in the compound, on the other hand, is found to shift towards lower energies by about 3.4 eV, with respect to the discontinuity in pure selenium.

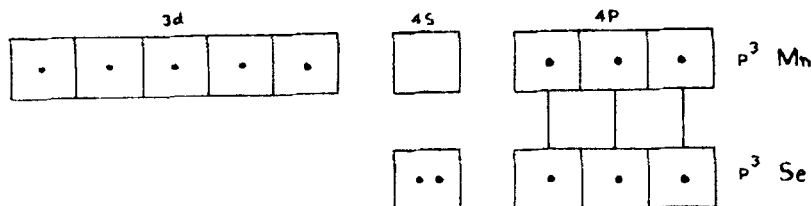


FIG. 3. Resonating p^3 type of bonding in MnSe.

The results of the measurements on the Mn K_{β_5} emission band are given in Table II. This band which appears to be somewhat broadened and diffused for the compound is found to shift by about 5.3 eV towards the high energy

side with respect to that in the pure metal. This shift can be seen in the spectra reproduced in Fig. 2.

TABLE I
Experimental data on the K absorption discontinuities

Absorber		λ X. U.	ν/R	Energy (E) eV
Manganese				
Mn metal (Bearden ⁶)	..	1891.30	481.82	..
Mn metal	1891.29 ± 0.06	481.82	6540.8 ± 0.5
MnSe	1889.66 ± 0.06	482.24	6546.4 ± 0.5
				$\Delta E_1 = 5.6$ eV
Selenium				
Se pure (Bearden ⁶)	..	977.80	931.96	..
Se pure	977.82 ± 0.07	931.94	12651.1 ± 0.5
MnSe	978.08 ± 0.07	931.59	12647.7 ± 0.5
				$\Delta E_2 = 3.4$ eV

TABLE II
Experimental data on the manganese $K_{\beta 5}$ emission band

		λ X. U.	ν/R	Energy (E) in eV
Mn metal (Bearden ⁶)	..	1893.20	481.34	6534.1
Mn metal	1892.01 ± 0.06	481.64	6538.3 ± 0.4
MnSe	1890.48 ± 0.06	482.03	6543.6 ± 0.4
				$\Delta E = 5.3$ eV

DISCUSSION

The crystal structure of MnSe has been studied by Baroni,⁷ who found three distinct structures α , β and γ for the compound depending upon the method of its preparation. Of these, the α -phase alone is stable and its structure is of the NaCl type. The β and γ phases are unstable, their structures being of the zincblende and wurtzite type respectively. These unstable forms go back eventually into the α -phase. According to Baroni, the value of ' a ' for the stable structure is 5.44 Å.

Considerable experimental work⁸ on the magnetic behaviour of MnSe at various temperatures has been done. It has been shown that the compound is antiferromagnetic in nature. The value of its magnetic moment, 5.7 B.M., at room temperature, shows that the number of free spin electrons in the d orbitals of the Mn atom in the compound is five.

To explain the chemical bonding in hexa-co-ordinated compounds with the simple formula TX (Here T stands for the transition metal and X for the metalloid atom), Pearson¹ has utilised the idea of electron promotion, first suggested by Pauling.⁹ According to Pearson, a d electron and two s electrons of the transition metal atom are promoted to the higher p orbitals of the atom for the establishment of the formula s^0p^3 . The metalloid atom, on the other hand, donates a p electron to the metal atom, which occupies the hole created in the d orbital. The chemical bonding then takes place due to resonating p^3 bonds, thus satisfying the requirements of structure and co-ordination. We will now discuss our experimental results for MnSe in the light of this theory.

Following the theoretical and experimental work of Richtmyer *et al.*¹⁰ it is now generally accepted that the inflexion point on an X-ray absorption edge in the case of a metal represents the position of the Fermi limit. No theoretical calculations on the shape of the absorption discontinuities for semiconductors and insulators have yet been made. The experimental work of Deslattes and deBen¹¹ on the K emission and absorption spectrum of selenium, which is a semiconductor, shows that the midpoint of the emission edge coincides with the inflexion point of the absorption discontinuity. It may, therefore, be assumed that the inflexion point on the absorption edge of a semiconductor represents the top of the valence band. The electronic structures of manganese and selenium atoms can be written as $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$ and $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$. In manganese metal the outermost filled band consists of $3d$ and $4s$ electrons whereas in selenium the valence band is made up of the $4p$ electrons.

The observed shift of the Mn K edge in MnSe indicates a shift of the top of the filled band toward the high energy side. The shift of the Se K edge in MnSe, on the other hand, indicates the shift of the top of the Se valence band toward the low energy side. This latter shift suggests that a p electron of selenium is transferred into the manganese atom, as can be expected on Pearson's theory. The shift of the Mn K_{β_5} emission band brings a direct experimental evidence to show that the $4p$ orbitals of manganese are filled due to promotion of inner electrons as well as due to the transfer of a selenium p electron. These two facts together account for the shift of the Mn K edge in MnSe towards high energies. Thus our X-ray spectroscopic results confirm that the bonding in this compound takes place due to resonating p^3 bonds as shown in Fig. 3. The semiconducting property^{3, 12} of the compound may be attributed to this directional bonding.

As mentioned earlier, in Pearson's picture one p electron of the metalloid atom is transferred into the d orbitals of the metal atom. Alternatively, it can be imagined that only two s electrons of the metal atom are promoted to the p orbitals and that one p electron of the metalloid atom goes directly into the remaining p orbital of the metal atom, giving ultimately essentially the same picture with resonating p^3 bonds. Our experimental results confirm the final p^3 bonding picture, but are unable to show in which manner the electron transfer takes place. However, irrespective of this, the electron transfer shows that the bonding in the compound is of the iono-covalent type.

CONCLUDING REMARKS

In the foregoing section, we have shown how it is possible to interpret X-ray spectroscopic data to bring information on the chemical bonding in a typical intermetallic compound manganese selenide. In this particular case the only theoretically possible bonding has been very well confirmed by our work. However, for many other systems several types of bonding are theoretically possible. In such cases the X-ray spectroscopic technique may be helpful in arriving at the correct picture of chemical liaison. Experimental work in this direction is in progress and will be reported later.

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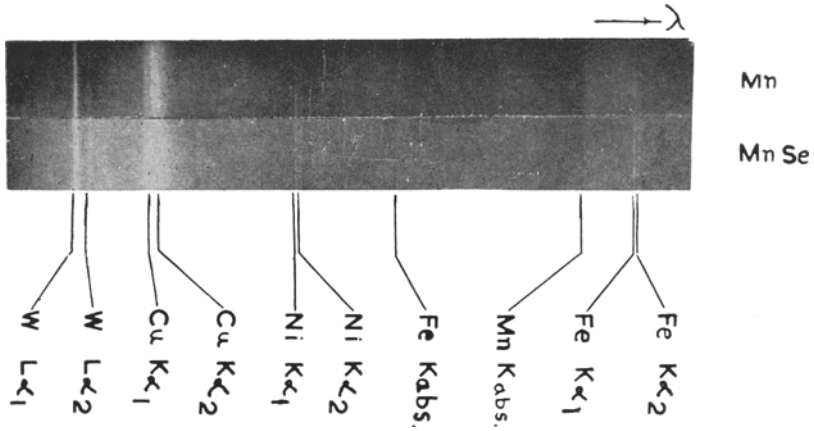


FIG. 1

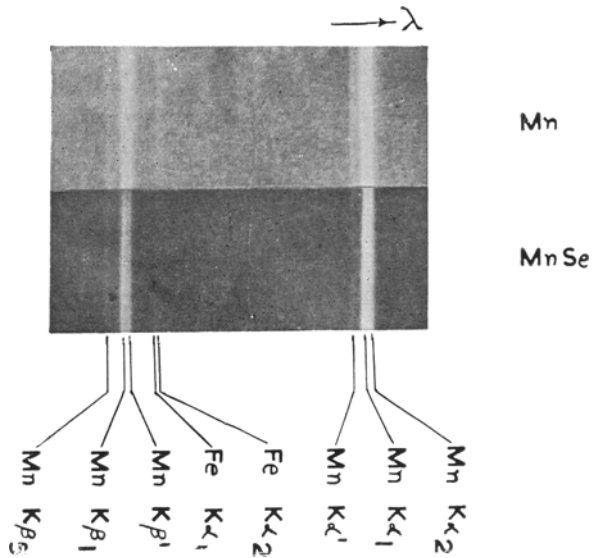


FIG. 2