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Abstract. The present authors have studied the Mn K absorption discontinuity in manganese and in two aluminium alloys of compositions Al–14.3 at.% Mn and Al–30 at.% Mn. It is found that the K absorption discontinuity of manganese shifts towards high energies for alloys with respect to that for the metal. The results are discussed on the basis of the rigid-band model.

1. Introduction

The subject of the electronic structure of alloys has attracted much recent interest [1, 2]. A large number of experiments have been carried out to investigate the electronic properties of alloys and several theories have been put forward in recent years [3–5] to account for their electronic structure. Of special interest are the non-magnetic transition-metal–aluminium alloys, such as the Al–Mn system.

When two metallic atoms are brought together in a solid, they form an intermetallic system. In an intermetallic compound, the valence electrons from one atom are transferred to the other whose electronegativity is higher. In such a case an iono-covalent bond is formed between the two atoms, which characterizes the bonding in the intermetallic compound. On the other hand, when the electronegativity difference between the two constituent atoms is not significant (about 0.5 or less), both the atoms may contribute their valence electrons to the electron gas in the solid, giving rise to delocalized, completely covalent metallic bonding, which is the characteristic of an alloy [6].

It is well known [7] that the investigations of x-ray absorption discontinuities provide valuable information about chemical bonding in intermetallic compounds. In some earlier publications from our laboratory [8, 9] we have shown how the rigid-band model can be used to explain the shifts of the x-ray absorption discontinuities in alloys of noble metals. In the present work we have studied the K absorption discontinuity of manganese for the pure metal and for two Al–Mn alloys to see whether this model can be extended to such a system.

2. Experimental details

A Cauchois-type bent-crystal x-ray spectrograph of diameter 0.4 m was used to photograph the Mn K absorption spectra. The spectrograph was equipped with a well tested

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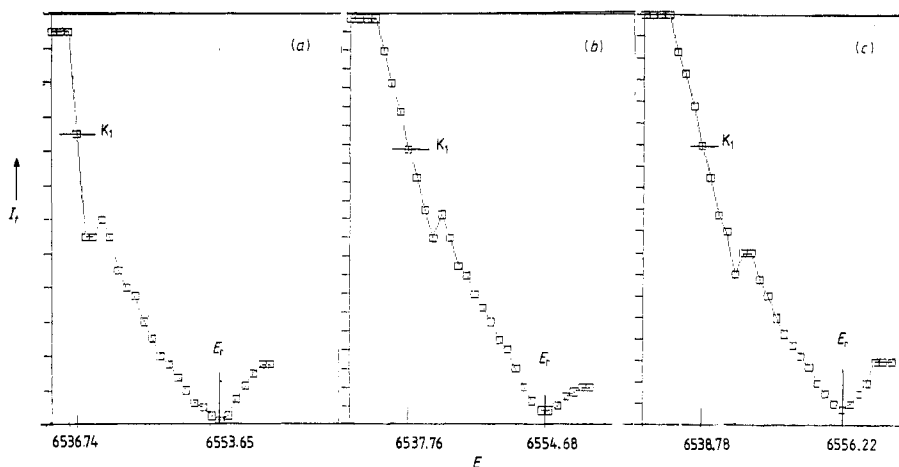
Figure 1. Mn K absorption discontinuity for (*a*) manganese metal, (*b*) the alloy with 14.3 at.% Mn and (*c*) the alloy with 30.0 at.% Mn.

mica crystal whose (100) reflecting planes were used to obtain the spectra. A sealed Chirana x-ray tube with tungsten anode, operated at 20 kV and 10 mA, was used as the source of white radiation. The spectra were photographed on Orwö blue-based fine-grain films which were developed in freshly prepared developer at 20 °C, taking utmost care to avoid any shrinkages in the development process. Microdensitometer data were obtained on a computer-controlled Joyce Loebl microdensitometer. The Fe $K\alpha_1$ and Fe $K\beta_{1,3}$ emission lines, whose energies were taken from the tables of Cauchois and Sénémaud [10], were used as reference lines for the energy measurements. The intrinsic energy resolution of our spectrograph with a mica(100) crystal, at the Mn K absorption discontinuity, is less than 2 eV, as calculated theoretically [11] as well as determined experimentally by measuring the full widths at half-maximum (FWHMs) of the Fe $K\alpha$ emission lines. The details of the spectroscopic technique can be found elsewhere [12].

The Al–Mn alloys with 14.3 at.% Mn and 30 at.% Mn were prepared using the roller-quenching technique. The alloys were then annealed in evacuated quartz ampoules and were characterized using the energy-dispersive x-ray analysis and differential thermal analysis (DTA) techniques. The DTA studies revealed that the alloys with 14.3 at.% Mn and 30 at.% Mn are very similar to the stoichiometric alloy phases Al_6Mn and δ-Al–Mn ($Al_{11}Mn_4$), respectively.

3. Results

It is well known that the inflection point on the x-ray absorption discontinuity corresponds to the Fermi level in the case of metals and alloys [13]. In our work the K absorption discontinuity of manganese is found to be split into two components K_1 and K_2 for the pure metal as well as for the alloys as can be seen in figure 1 in which the transmitted x-ray intensity I_t is plotted against the incident photon energy E. The measurements on the principal K absorption discontinuity K_1 of manganese for the pure metal and for the alloys, which gives the position of the Fermi level, are given in

Table 1. Fermi level shifts.

Sample	Experimental		Theoretical	
	Energy of $K_1 \pm 0.5$ (eV)	Experimental shift $(\Delta E)_{exp}$ (eV)	Fermi energy E_F (eV)	Theoretical shift $(\Delta E)_{th}$ (eV)
Mn metal	6536.74	—	10.91	—
Al–14.3 at.% Mn	6537.76	1.02	11.97	1.06
Al–30.0 at.% Mn	6538.78	2.04	12.99	2.08

table 1. It is seen from this table that the Mn K absorption discontinuity in the alloys shifts progressively towards higher energies as the concentration of manganese in the alloys increases.

4. Discussion

It has been shown [7, 14] that the chemical shifts of the x-ray absorption discontinuities in compounds are governed by the nature of the chemical bonding, and in particular by the effective charges on the absorbing atoms. It is found that, whenever the absorbing atom is a cation, the x-ray absorption discontinuity shifts, with respect to that of the pure metal, towards higher energies and, when the absorbing atom is an anion, it shifts towards lower energies. In a binary compound, the more electronegative atom should behave as an anion while the less electronegative atom as a cation. In the case of the Al–Mn system, the electronegativity difference is zero according to the Pauling [15] scale, 0.13 according to the Allred–Rochow [16] scale and 0.27 according to the Mande *et al* [17] scale.

According to Mullay [18] the electronegativity scale due to Mande *et al* which is based on x-ray spectroscopy measurements is more reliable for the transition-metal series.

As the electronegativity difference in all these scales is less than 0.5, it is not expected to play an important role in bonding. In any case, according to the electronegativity criterion the Mn atom should behave as an anion in these materials. This is very unlikely since the Mn K absorption discontinuity for the alloys is found to shift towards higher energies with respect to that for the pure metal. The difference in the electrochemical potential φ on the scale given by Miedema [19] is quite small (0.25) and therefore this criterion is also not helpful in distinguishing between the anion and the cation in the Al–Mn system. These considerations lead us to believe that the bonding in these materials is not of the iono-covalent type. The only alternative seems to be to consider metallic bonding in them. Furthermore in the case of aluminium–manganese alloys, the electrical resistivity value [20] of the stoichiometric phases is almost the same as that for pure aluminium, which leads us to believe that the alloys are metallic in character. We shall therefore attempt to apply the rigid-band model to these alloys to see whether the observed shifts can be explained by this model.

Many experiments in x-ray absorption spectroscopy have led to the conclusion [7] that the inner levels are not appreciably perturbed by chemical bonding. The outermost

levels, which participate directly in bonding, are affected by the environment, which gives rise to shifts of the x-ray absorption discontinuities. Some photoelectron spectroscopic results also seem to indicate that [21–23] the core level shifts in alloys are negligible in comparison with those of the outermost levels. Assuming therefore that the effect of the environment on the core level of the absorbing atom is relatively small, we shall try to correlate the observed shifts of the position of the principal discontinuity of Mn for the Al–Mn alloys with respect to that for the pure metal with the changes in the position of the Fermi level, in the light of the rigid-band model.

In the rigid-band model, in an alloy the valence electrons of the constituent metal atoms form a conduction band whose width can be calculated from the Fermi–Sommerfeld free-electron theory of metals [24]. According to this theory the energy E_F^{metal} of the Fermi level in a metal is given by

$$E_F^{metal} = (h^2/2m)[(3/4\pi)(N/gv)]^{2/3} \tag{1}$$

where h is the Planck constant, m is the free-electron mass, N is the number of free electrons per unit cell, g is the degeneracy factor and v is the volume of the unit cell.

Since for the free electrons the degeneracy factor g is taken as two, and putting $n = N/v$, we obtain from equation (1)

$$E_F^{metal} = (\hbar^2/2m)(3\pi^2 n)^{2/3} \tag{2}$$

where $\hbar = h/2\pi$ and n is the number of free electrons per unit volume.

The above equation can be modified for an alloy as

$$E_F^{alloy} = (\hbar^2/2m)(3\pi^2 n')^{2/3} \tag{3}$$

where n' is the number of free electrons in the alloy per unit volume.

The theoretical shift of the Fermi level accordingly is

$$\Delta E_F = E_F^{alloy} - E_F^{metal}. \tag{4}$$

In α-Mn, which has been used in this work, the density is 7.743 g cm^{-3}, the unit-cell volume [25] is 707.82 Å^3 and each Mn atom donates two valence electrons to the electron gas [26]. From these values we obtain the number n of free electrons per unit volume to be 16.38×10^{22} electrons/cm^3 in manganese metal. Substituting this value in equation (2) we obtain a value for the Fermi energy in α-Mn of 10.91 eV.

Nemoshkalenko *et al* [27] have studied several Al–Mn alloys by the soft x-ray emission spectroscopy technique. Their studies reveal that the electronic configuration of the Mn atom in these alloys is close to $3d^{4.5}4(sp)^{2.5}$, which implies that each Mn atom donates 2.5 electrons to the conduction band in an alloy.

For the alloy with 14.3 at.%Mn, which is close to the stoichiometric phase Al$_6$Mn we can use the crystallographic data for Al$_6$Mn to calculate the Fermi level using equation (3). The crystallographic study of Nicol [28] gives the volume of the Al$_6$Mn unit cell as 435.27 Å^3. The unit cell contains 24 aluminium atoms and four manganese atoms. Since each aluminium atom contributes three valence electrons to the conduction band in the alloy while each manganese atom in the alloy donates 2.5 valence electrons (as per the suggestion of Nemoshkalenko *et al*) the total number n' of free electrons per cubic centimetre turns out to be 18.84×10^{22} cm^{-3}. Substituting this value in equation (3) we get the value of the Fermi level in the alloy as 11.97 eV.

To calculate the Fermi level in the alloy with 30 at.% Mn, which is close to the stoichiometric phase δ-Al–Mn or Al$_{11}$Mn$_4$, we can make use of the crystallographic work of Bland [29], which gives the unit-cell volume to be 432.19 Å^3. The unit cell

contains 32 atoms, out of which 24 atoms are of aluminium and eight of manganese. Therefore the total number of free electrons per unit volume turns out to be 21.29×10^{22} cm^{-3}. Substituting this value in equation (3) we obtain a value of 12.99 eV for the Fermi level of this alloy.

The theoretical shifts based on the rigid-band model are thus found to be 1.06 eV and 2.08 eV for the alloys with 14.3 at.% Mn and 30 at.% Mn, respectively. These values are in good agreement, both in sign and in magnitude, with the experimentally observed shifts, as can be seen from table 1.

Ichikawa [30], has studied the soft x-ray $L_{2,3}$ emission spectra of aluminium in dilute Al–Mn alloys. His work shows that, when the concentration of manganese is less than 20 at.%, the Fermi level does not show any marked change with respect to that of pure aluminium. The calculated energies of the Fermi level of aluminium metal and of the alloy with 14.3 at.% Mn are found to be 11.64 eV and 11.97 eV, respectively, which are quite close to each other. One cannot therefore expect to observe experimentally any shift in the Fermi energy of dilute alloys with respect to that of pure aluminium.

5. Concluding remarks

Our work shows that one can make use of the rigid-band model to interpret x-ray absorption and emission spectra in non-magnetic transition-metal alloys. The application of this model to the transition-metal alloys in general is difficult because of the presence of the transition-metal atom which complicates the electronic structure. In particular, it is not always clear how many electrons are donated by the transition-metal atom to the conduction band of the alloy; this information is necessary to calculate the Fermi level. Our work seems to support the conclusion arrived at earlier by Nemoshkalenko *et al* that 0.5 electrons per atom are transferred from the manganese d band to its sp band in these materials.

Acknowledgments

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