CHARGE TRANSFER AND ATOMIC VOLUME EFFECT IN FexSn1-x AMORPHOUS ALLOYS

M. Piecuch, Chr. Janot, G. Marchal

To cite this version:
M. Piecuch, Chr. Janot, G. Marchal. CHARGE TRANSFER AND ATOMIC VOLUME EFFECT IN FexSn1-x AMORPHOUS ALLOYS. Journal de Physique Colloques, 1980, 41 (C1), pp.C1-251-C1-252. 10.1051/jphyscol:1980184 . jpa-00219777

HAL Id: jpa-00219777
https://hal.archives-ouvertes.fr/jpa-00219777

Submitted on 1 Jan 1980

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
I - INTRODUCTION.

Amorphous alloys have been obtained over a wide compositional range and thus have provided a good opportunity of studying in details electronic properties of alloys. The old controversy of the charge transfer has been reopen recently in attempts to understand the magnetic behaviour of amorphous alloys made of transition metals MT and metalloids Me (MT, Me, 1-x). Obviously, magnetization measurements /1/, in particular the existence of a critical value \( x_c \approx 0.4 \) for the appearance of magnetic interactions /2/ are in favour of a progressive filling of the 3d states of MT by transfer from the metalloid s-like band. However, band structure calculations in the Fe-3Si crystalline compound /3/ have shown that the sp state energy is lower than that of the Fe-3d states, making impossible any charge transfer /4/.

On the other hand the critical composition can be interpreted in terms of several different models /2/ including a localized model /5/ which is an extension of that once proposed by Jaccarino and Walker /6/.

The \( \text{Fe}_x\text{Sn}_{1-x} \) amorphous alloys is a good candidate to make valuable contribution to this charge transfer problem since electron density measurements can be carried out simultaneously on \(^{57}\text{Fe} \) and \(^{119}\text{Sn} \) nuclei using Mössbauer spectroscopy. Details about preparation, electrical resistivity measurements, density data, magnetization values and Mössbauer experiments in these amorphous alloys have been extensively reported elsewhere /2/ /7/ /8/ /9/ /10/ and this present paper will concentrate on the interpretation of isomer shift data.

II - EXPERIMENTAL RESULTS.

Mössbauer spectra measured at RT on \(^{119}\text{Sn} \) and \(^{57}\text{Fe} \) isotopes can be mainly described in terms of broad, more or less asymmetrical sextuplets for \( \text{Fe}_x\text{Sn}_{1-x} \) alloys in their magnetic form. As explained elsewhere /11/ a composition dependent mean isomer shift can be defined for both tin and iron and determined from the geometrical centroid of the spectra. These mean isomer shift data are presented in figure 1 along with results obtained from crystalline iron-tin compounds /12/ and \( \text{Cu}_x\text{Sn}_{1-x} \) amorphous alloys /13/. Thus in alloys of the iron-rich side the electronic density is larger near iron and lower near tin atoms than in the alloys of the other side.

![Fig. 1](https://example.com/fig1.png)

Composition dependence of the mean isomer shift measured on \(^{57}\text{Fe} \) (a) and \(^{119}\text{Sn} \) (b) \((\bullet)\) in \( \text{Fe}_x\text{Sn}_{1-x} \) amorphous alloys. Full lines: calculated values; \( \times \) CuSn amorphous alloys /13/; \( \uparrow \) crystalline iron-tin compounds /12/.

III - INTERPRETATION AND DISCUSSION.

Changes in electronic density may arise from atomic volume effect and charge transfer effect. Thus this section will try to analyse the relative contribution of both effects.

According to Watson et al. /14/, a mean atomic volume in binary amorphous alloys is given by the expression:

\[
\langle N_{at}(x) \rangle = \frac{\langle N(x) \rangle}{\langle d(x) \rangle}
\]

with \( \langle M(x) \rangle = x M(\text{Fe}) + (1-x)M(\text{Sn}) \) in which \( M(\text{Fe}) \) and \( M(\text{Sn}) \) are the molecular weight of iron and tin; \( \text{d} \) is the Avogadro number and \( d(x) \) the weight density of the alloys as measured in ref. /7/. The experimental data shows a linear composition dependence of \( \langle N_{at}(x) \rangle \) in \( \text{Fe}_x\text{Sn}_{1-x} \) amorphous alloys. This is an experimental evidence that the mean atomic volumes of both Sn and Fe are mostly constant whatever the alloy composition. However, it is worth noting that this constancy may result from local fluctuation averaging to zero in space. Fitting the data with the formula:
\[ \langle \psi^\prime_{\text{ac}}(x) \rangle = x \tilde{\psi}(\text{Fe}) + (1-x) \chi(\text{Sn}) \]

leads to:
\[ \tilde{\psi}_{\text{ac}}(\text{Fe}) = 15.7 \text{ Å}^3 \]
\[ \chi_{\text{ac}}(\text{Sn}) = 24.6 \text{ Å}^3 \]

To be compared with \( \psi_{\text{ac}}(\text{Fe}) = 11.7 \text{ Å}^3 \) in the bcc crystalline structure and \( \psi_{\text{ac}}(\text{Sn}) = 27 \text{ Å}^3 \) in the tetragonal structure of \( \beta\)-tin. Thus changes in isomer shift values have to be ascribed to charge transfer only. The general formula for isomer shift can be written:
\[ \delta = \delta_0 + \alpha \Delta \rho(o) \tag{1} \]

in which \( \delta_0 \) is the isomer shift in a reference material and \( \rho(o) \) is the electronic density at the nucleus.

In iron compounds, \( \rho(o) \) includes contributions from core electrons \( \rho_c(o) \) and conduction band electrons \( \rho_b(o) \). According to Ingalls et al. /15/
\[ \rho_c(o) = -5n_o^{-3} n_{3d} \]
\[ \rho_b(o) = +8.3a_o^{-3} n_{4s} \]

in bcc \( \alpha\)-Fe. In a close packed structure like \( \varepsilon\)-Fe or amorphous alloys, \( \rho_b(o) \) is still the same but \( \rho_c(o) \) should be slightly larger. However there is an opposite variation in amorphous alloys coming from the atomic volume increasing from 11.7 \( \text{Å}^3 \) (\( \alpha\)-Fe) to 15.7 \( \text{Å}^3 \). As a reasonable estimate \( \rho_b(o) \) will be taken around 7 \( a_o^{-3} n_{4s} \). Thus isomer shift of iron amorphous compound may be given by the expression:
\[ \delta(\text{Fe} \gamma) = \delta_0 - \alpha [7 \Delta n_{4s} - 5 \Delta n_{3d}] \tag{2} \]

in which \( \alpha \) is a positive constant of the order of 0.23 \( a_o^{-3} \text{mm} \cdot \text{sec}^{-1} /16 \).

In tin compounds there is still some controversy about the \( \alpha \) coefficient (Eq. 1) which is found around 0.05 \( a_o^{-3} \text{mm} \cdot \text{sec}^{-1} \) when obtained from calculated relativistic wave functions or near 0.1 \( a_o^{-3} \text{mm} \cdot \text{sec}^{-1} \) if deduced from electron conversion experiments /17/. In this paper \( \rho_{\text{Sn}}(o) \) has been calculated using the De Vries et al. /18/ wave functions and consequently \( \alpha \approx 0.05 a_o^{-3} \text{mm} \cdot \text{sec}^{-1} \), thus leading to the expression:
\[ \delta(\text{Sn} \kappa) = \delta_0 + 1.09 \Delta n_{5g} \tag{3} \]

The electronic density at \( 119\text{Sn} \) nucleus is larger in amorphous than in crystalline material, despite a bigger atomic size; it must be ascribed to reducing in covalency effect. Thus we will assume that an ideal amorphous pure tin metal would have a \( 5s^2 \cdot 5p^2 \) configuration and then \( \delta_0 (a-\text{Sn}) \approx 3.27 \text{ mm} \cdot \text{sec}^{-1} \) (with respect to \( \text{BaSnO}_3 \)). In the same way, it can be assumed that an ideal amorphous pure iron metal would have the same electronic configuration than metallic \( \alpha\)-Fe, that is something like \( 3d^7 \cdot 5s^3 \cdot 5p^2 \cdot 5d^0 \cdot 5f^5 \), the difference in \( \rho_b(o) \) leading to an isomer shift of \( \delta_0 = +0.14 \text{ mm} \cdot \text{sec}^{-1} \) for pure amorphous iron with respect to crystalline \( \alpha\)-Fe.

Calculation of charge transfer is made here through a simple phenomenological approach within the following hypotheses:
- the Sn 4d states, being about 30 eV below the Fe 3d states, are completely filled;
- the electronic density in the conduction band has a constant homogeneous value inside the alloy; thus \( \tilde{\psi}_{\text{ac}}(\text{Sn}) = 2 \tilde{\psi}_{\text{ac}}(\text{Fe}) \) results in
\[ n_{5g}(\text{Sn}) = 2 n_{5g}(\text{Fe}) \]
- near the iron atoms the conduction electrons are mostly 4s like, that is \( n_{4s}(\text{Fe}) \approx n_{4s}(\text{Sn}) \)
- near tin atoms the conduction electrons are half 5s, half 5p-like, that is \( n_{5s}(\text{Sn}) = 2 n_{5s}(\text{Fe}) \)
- the average number of electrons transferred from sp tin band to 3d iron state is in proportion of tin concentration and the 2.5 holes in the 3d iron state are full up when an iron atom is surrounded by tin atoms only, so:
\[ \Delta n_{3d} = 2.5 \text{ (1-x)} \tag{7} \]

Equations (4), (5) and (6) results in \( n_{4s}(\text{Fe}) \) which gives:
\[ \Delta n_{3d}(\text{Sn}) = -1.5 + \Delta n_{4s}(\text{Fe}) \tag{8} \]

Using the expressions (7) and (8) in the electronic balance of the material:
\[ 8x + 6(1-x) = 2n_{5g}(\text{Sn}) - 6s(\text{Fe}) + n_{4s}(\text{Fe}) \]
leads to:
\[ \Delta n_{4s}(\text{Fe}) = 3 - 0.5x + 2.5x^2 \]
\[ \Delta n_{5g}(\text{Sn}) = 2.5x^2 - 4x \]

Putting these values in Eq.(2) and (3) along with \( \Delta n_{3d}(\text{Fe}) \) (Eq.7) gives:
\[ \left\{ \begin{array}{c}
\delta(\text{Sn}) = 3.27 + 1.09 \frac{2.5x^2 - 4x}{2 - x} \text{ (mm} \cdot \text{sec}^{-1}) \\
\delta(\text{Fe}) = 0.14 - 0.23 \frac{3 - 0.5x + 2.5x^2}{2 - x} \text{ (mm} \cdot \text{sec}^{-1})
\end{array} \right. \]

The agreement with experimental data is quite reasonable in figure 1.

REFERENCES

/7/ (a) MARCHAL G., MARCHAL P., PIECHOW M., KELNYI D. and JANOT Ch., Proc. of the 3rd Int. Conf. on rapidly quenched metals (Brighton) 1 (1978) 72.
/10/ ROMAINE D.S., PIECHOW M., JANOT CH., MARCHAL G. and MARCHAL PH., Rev. (to be published).
/13/ BOULJ J. and POOLE F., Zeits. Phys. 175 (1955) 95.