ISOMERIC CHEMICAL SHIFTS FOR TIN ALLOYS WITH d-METALS

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

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ISOMERIC CHEMICAL SHIFTS FOR TIN ALLOYS WITH *d*-METALS

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The magnitude of the isomeric chemical shift δ is readily determined from the relative position of the Mössbauer lines of the absorber and the source. This quantity is proportional to the change in the electron density in the region of the nucleus $|\psi(0)|^2$ in the absorber atoms as compared with the source atoms, and to the change in the nuclear radius in the transition from the ground to the excited state. Thus, the information obtained pertains both to the nucleus and to the distribution of electrons in a solid. Such important properties of δ have led to the need for a systematization of the magnitudes of isomeric chemical shifts. For example, V. I. Gol' danskii (^{1}) placed the isomeric chemical shifts of tin and iron compounds on a number scale; often δ is represented as a function of electronegativity (^{1}-^{3}) or of the degree of ionicity of the bond; there are correlations with the introduced characteristic $\theta_0^2 m_0$ (^{4}), etc.

Fig. 1. Illustration of the linear dependence $\delta(C)$ in the systems: Co–Sn, Ni –Sn, Pd–Sn, Pt–Sn, Rh–Sn. a –our measurements, b –literature data

Fig. 2. Experimental values of $\delta(C)$ for tin alloys with d-metals for the same composition have close values. a –our measurements, b –literature data

We carried out a study of Mössbauer spectra for a number of compounds of tin alloys with elements of Group VIII: Co, Ni, Rh, Pd, Pt. The phases were identified by X-ray diffraction; only those compounds for which complete agreement with the literature data was observed were investigated for the Mössbauer effect (^5). The experimental values obtained for the isomeric chemical shifts δ were plotted for each binary system as a function of the atomic concentration C of tin in the alloy. The dependence $\delta(C)$ proved to be close to linear (see Fig. 1). For the Pd—Sn system such a dependence had been found by us earlier (^4). In Fig. 2 all our experimental results are brought together, supplemented by literature data taken from the review paper (^1). The location of the experimental points $\delta(C)$ within a narrow band reflects the identical nature of the chemical bond in the alloys studied. Thus, the linear dependence established in this work of the isomeric chemical shift on atomic concentration is apparently universal, at least for metallic systems of tin with d-metals.

This result is easy to explain. When a solid is formed, the valence $5s$-electrons of tin are no longer bound in the orbitals of a free atom, but occupy states of the entire crystal. For small concentrations of tin, the most probable process is the transition of the valence electrons into the conduction band of the alloy, which corresponds to a "smearing out" of their wave functions over the whole crystal. As the concentration of tin atoms in the alloy increases, their individual properties begin to appear, which leads to the formation of compounds with a determining influence of tin atoms on the chemical bond. In accordance with this process, a linear change occurs in the electron density at the tin nucleus as a function of the atomic concentration of the alloy.

The normalization of the wave function $|\psi_s(0)|^2$ proposed by us in work (^6) is confirmed by the general regularity found here, but it must be remembered that its application is possible only for metals and alloys in which the crystal lattices approach close packings and the collective properties of the electrons are most strongly expressed.

When considering nonmetallic tin compounds, in analyzing isomeric chemical shifts one must take into account the atomic-crystal structure of the compounds and, first of all, the interatomic distances and coordination. For complex compounds with directed chemical bonding, at one and the same valence state of the tin atoms the density $|\psi(0)|^2$ may prove to be different because of the unequal displacement of the energy levels of the deep-lying s-electrons.

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Note: Figure translations are in progress. See original paper for figures.