

EFFECT OF IMPURITIES ON ISOMER SHIFTS IN METALLIC TIN

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The effect of impurities on isomer shifts in metallic tin are studied. It is shown that even a small amount of an impurity with valence s electrons changes the magnitude of the isomer shift in the host nuclei.

WHEN the Mössbauer effect is studied in impurities added to metals or alloys, changes in the properties of the host are customarily ignored because of the small content ($\sim 1\%$) of investigated impurity atoms. The correctness of this procedure has not hitherto received detailed experimental verification.

In the present work we have determined the isomer shifts for Sn^{119} in natural (metallic) tin to which Na, Zn, Cd, Ge, In, Sb, Pb, or Bi was added as an impurity. The source of resonant γ radiation was $\text{Mg}_2\text{Sn}^{119*}$; the source and absorber were maintained at liquid nitrogen temperature. The alloys were prepared within a quartz ampoule in an argon atmosphere; alloys containing the maximum possible impurity content were prepared first, the initial concentration being a little under the limit of solubility. Alloys with smaller impurity concentrations were then prepared by successive dilutions. The absorber foils were rolled and annealed. High-purity tin containing at most 5×10^{-4} at. % impurities was used. The foils were of identical thickness.

In all cases the absorption spectra consisted of singlet lines with half-widths that did not differ appreciably from those of pure tin having the same thickness. The shift was determined from the difference in the counts N at source velocities v corresponding to the maximum slope of the pure-tin absorption line,^[1, 2] and was also checked by determining the absorption-line center of gravity for the impure tin.

Figure 1 shows the absorption spectra for pure β -Sn and for tin containing 0.5 and 1 at. % Zn. These spectra show qualitatively that a relatively small amount of impurity has some effect on the density of s electrons in tin nuclei. However, the impurities do not all have the same effect with regard to isomer shifts.

Figure 2 shows the dependence of the isomer

shift δ (relative to metallic tin) on the impurity concentration. Within experimental error limits the presence of Ge, Pb, In, Sb, and Bi in tin has no effect on the isomer shift for the entire range of solid solutions. With Zn or Cd the isomer shift for tin nuclei is enhanced; beginning with a concentration ≈ 0.5 at. % the shift remains approximately constant at 0.06 ± 0.02 mm/sec. The pattern is similar for the Na impurity, but the isomer shift lies systematically between the shifts for pure tin and tin doped with Zn or Cd.

The change of the isomer shift for the tin nuclei that occurs upon the addition of Zn or Cd atoms,

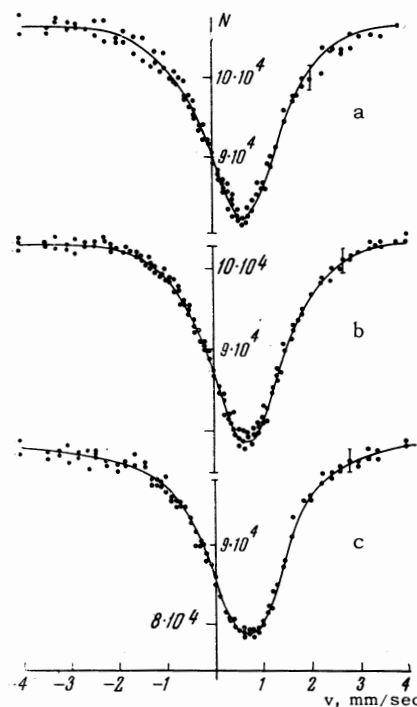


FIG. 1. Absorption spectrum of (a) pure metallic tin, (b) tin containing 0.5 at. % Zn, and (c) tin containing 1 at. % Zn. The source was $\text{Mg}_2\text{Sn}^{119*}$.

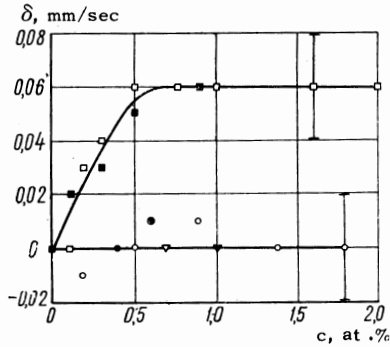


FIG. 2. Isomer shift δ (relative to βSn) for Sn^{119} nuclei in metallic tin containing Zn (\square), Cd (\blacksquare), Ge (\bullet), In (\circ), Sb (\blacktriangledown), Pb (∇), and Bi (\circ) versus impurity concentration c .

whose outer shells are occupied by s electrons in the isolated state, could result from the scattering of conduction electrons on charged impurity centers. Because of their electronegativity Na, Zn, and Cd easily transfer their valence s electrons to the total conduction band, thus leaving ions with unoccupied valence s levels. Then the largest cross section for scattering on Na, Zn, and Cd ions belongs to the conduction electrons with a finite probability of being in the neighborhood of one of these nuclei; these are the conduction electrons that contribute to isomer shifts. If an impurity should give up its valence p electrons to the total conduction band (as is possible for Ge, Pb, In, Sb, and Bi), the resonant scattering efficiency would be enhanced for the conduction electrons having a small probability of being in the neighborhood of the nucleus and therefore having practically no effect on the isomer shift.

It is also possible that Ge, Pb, In, Sb, and Bi do not transfer valence electrons to the total conduction band so readily as Na, Zn, and Cd, since there is only a small difference between the electronegativities of tin and the Ge, Pb, In, Sb, or Bi impurity atoms. Therefore these impurities would have only a small perturbing effect on the conduction electrons.

In a region about an impurity center the wave functions of conduction electrons are perturbed by scattering. The excess electron density $\delta n(r)$ in the vicinity of the impurity will be represented by^[3]

$$\delta n(r) = Ar^{-3} \cos(2k^0 r + \varphi), \quad (1)$$

where r is the distance from the impurity atom, k^0 is the Fermi wave number, and φ is the phase. The magnitudes of A and φ are expressed in terms of the phase shifts η_e for electrons scattered on the Fermi surface.

The perturbed region is relatively large, comprising several tens of atoms for the case of impurities in copper.^[3] Hence the initial rise of the curve in Fig. 2 can apparently be attributed to an increase in the number of regions with perturbed electron density. As a result the resonance line is split into approximately two families of lines, one of which corresponds to nuclei in regions with undisturbed or relatively undisturbed electron density, while the other corresponds to regions with considerable perturbation of the electron density. There is little difference between the isomer shifts of these lines. We therefore observe a single resonance line whose isomer shift depends on the size of its second component, i.e., on the number of disturbed regions. With increasing impurity concentration a limit is reached when the electron density is perturbed in practically the entire volume of the metal. For tin this appears to occur at ~ 0.5 at.%, when further change of the isomer shift becomes less noticeable.

The foregoing explanation is, of course, neither final nor unique; it is based on our experimental results, which indicate the existence of long-range interactions between impurity and host atoms, resulting in appreciable perturbation of the electron density in a metal or alloy and thus affecting the isomer shift. Therefore when the properties of metal lattices are investigated by means of the Mössbauer effect for impurity atoms the impurity concentration cannot be taken arbitrarily in the general case. Also, there is the possibility of an effect due to a difference between the valences of the impurity and the host (an effect that has been known for a long time), and to the s or p (or also d) symmetry of valence electrons belonging to the host and impurity atoms.

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