INTERPRETATION OF THE ISOMER (CHEMICAL) SHIFT OF THE MOSSBAUER ABSORPTION SPECTRA FOR Sn^{119} AND Au^{197} IMPURITY NUCLEI IN METALLIC MATRICES

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Isomer shifts for the Sn^{119} and Au^{197} impurity atoms are considered on the basis of the Goodings-Mozer formula, which expresses the charge density at impurity nuclei in metals in terms of the state density of the unperturbed matrix and of the magnitude of the perturbation. In the first case the variation of the isomer shifts can be explained by assuming an appreciable localization of the 5s level in the impurity position. In both cases the role of the difference between the valences of the impurity and the matrix is greater than the density of the unperturbed-matrix states.

AN investigation of the impurity states in metals occupies an important place in the physics of the condensed state of matter. In particular, the determination of the electron density at the impurity nuclei can be carried out experimentally either with the aid of the Knight shift by the method of nuclear magnetic resonance, or the isomer (chemical shift) of the Mossbauer gamma-quantum absorption spectra. Unfortunately, there is still no detailed theoretical interpretation of the isomer shift for impurity atoms in metallic systems (with allowance for the interaction of the impurities, for the screening of the impurity by the s-, p-, and d-like electrons, and also the changes of the electronic properties of the matrix when impurities are introduced in it), and only now is the process of accumulation of experimental data being essentially completed for the Mossbauer nuclei Fe^{57} and Sn^{119}. (The greatest progress has been reached in the understanding of the nature of the isomer shift for Fe^{57} impurity nuclei[1].) Therefore the possibilities of using the Mossbauer effect on impurity nuclei for the study of the properties of the conduction band of disordered systems have not been revealed to any degree at all. In solving such a problem, it is necessary first of all to determine the contribution made to the isomer shift by the conduction band of the matrix. In turn, this would extend the possibility of taking into account the contribution from the conduction electrons, for example, to the magnetic fields at the impurity nuclei. The connection of the isomer shifts for the impurity nuclei Sn and Au with the compressibility of matrices (see[2]) provides no answer to these questions.

In the present paper we attempt to consider qualitatively, on the basis of the available experimental data, this problem for impurity nuclei Sn and Au in metallic matrices from a unified point of view.

Let us consider first the case of Sn impurity nuclei. It was determined in a number of papers[3] that in the region of solid solutions of binary systems of Sn with other metals, the isomer shifts for the impurity nuclei Sn^{119} are practically constant. Therefore, when the stable isotope Sn^{119} was used as the impurity, they were determined at an impurity content ≈ 1 at.%, inasmuch as at this Sn content in the alloy the Mossbauer absorption

of the gamma quanta is noticeable and sufficient for an experimental determination of the parameters of the spectra. But such an impurity content is rather large, and the question is raised of the degree of interaction of the impurities with one another and with the atoms of the matrix, and the influence of these interactions on the parameters of the Mossbauer spectra. From the fact that the isomer shift for the Sn^{119} nuclei remains unchanged in the region of metallic solid solutions of binary systems, it still does not follow that the impurity Sn atoms do not interact with one another, since a similar dependence can be due to the insufficient sensitivity of the Mossbauer effect, when the interaction between the impurities affects essentially the collectivized 5p-like states of the impurity Sn. Even if the 5p-electrons of the impurity appreciably screen the 5s electrons, the degree of screening may remain approximately constant when the impurity concentration is increased, since the broadening and the downward energy shift of the impurity band act in this case in opposite directions on the charge density in the nucleus.

The isomer shift for the impurity nuclei Sn^{119} in Pd following the hydrogenation of the latter turned out to be practically equal for the solid solution and for the intermetallic compound of Pd with H, which have different lattice constants[4], thus demonstrating the low sensitivity of the isomer shift for the case of impurity Sn in a transition metal to the change of the lattice constant on the matrix and of its band structure. The isomer shift for impurity nuclei Sn^{119} in normal metals turns out to be proportional to the atomic volume of the matrix and also apparently little sensitive to the singularities of their band structures. The isomer shifts at Sn impurity concentrations near 1 at.% have values corresponding to the divalent state of Sn.

The aggregate of these factors makes it possible to advance the assumption that in all the cases under consideration of impurity Sn, its valent 5s-level is localized to a considerable degree in the impurity cell, and therefore the contribution from the band states is small. The localization of the 5s-states of Sn in monovalent matrices can be due to the fluctuation accumulation of impurity[5], in polyvalent matrices the small differences of the valences V of the impurity and the matrix can

come additionally into play, and in transition metals it may be due to the large density of the states in the conduction band of the matrix, leading to almost complete screening of the Sn in the impurity cell.

Consequently, the isomer shift of the Mossbauer absorption spectra for impurity nuclei should be determined by the contributions made by the local and virtual states of the impurity. For the case of one band taking part in the screening of the impurity and of the impurities that do not interact with each other, and for a perturbation localized in the volume of the impurity cell, the charge density at the impurity nuclei has, according to Goodings and Mozer[6], the form

$$\rho = 2|W(0)|^2 \left\{ \int_{-\infty}^{E_F} \frac{Vg_0(E)dE}{[1+UVF_0(E)]^2 + [\pi VUg_0(E)]} + \left[U^2 \int_{-\infty}^{\infty} \frac{Vg_0(E)dE}{(E-E_0)^2} \right]^{-1} \right\},$$

where $|W(0)|^2$ is the square of the modulus of the Wannier function for electrons in the position of the impurity nuclei, V is the atomic volume of the impurity, U is the value of the perturbation, $VF_0(E)$ is the principal value of the integral

$$\int_{-\infty}^{\infty} \frac{Vg_0(E')dE'}{E'-E}$$

g_0 is the density of states for one spin direction, and E_0 is the position of the local level. The first term in this expression is due to the virtual states and the second to local states. The expression in the curly brackets describes the influence of the matrix on the charge density at the impurity nucleus.

Although no account is taken of the interaction of the impurities in the expression for ρ, we shall nevertheless attempt to analyze on this basis the experimental data on the isomer shifts for the impurity nuclei Sn[119] in metallic matrices, inasmuch as we know that the Goodings-Mozer formula is the only one in which the charge density at the impurity nuclei is connected with the density of the states in the conduction band of the pure matrix, and at the same time no attempts were made to compare it with the experimental data. If an appreciable fraction of the charge density at the impurity nuclei Sn[119] is due to the local 5s-state, then it can be assumed that the character of the interaction of the impurities (if the interaction exists) is approximately the same in the sense that if affects principally the 5p-like states. Let us take into account the possible change of the atomic volume of the impurity in different matrices, assuming that the change of the atomic volume of the impurity is proportional to the atomic volume of the matrix. There are no published experimental data on $g_0(E)$ for metals, so that there is only one possibility—to use the values of the coefficient of the electronic specific heat γ, which is proportional to the density of the states at the Fermi level. When the impurity is introduced into the metal, the density of the states in the conduction band of the matrix changes, but we shall neglect this change, since, for example for the case of Ag, the presence of 1 at.% of Sn impurity changes the value of the electronic specific heat coefficient by only 0.5%[7].

Figure 1 shows the values of the isomer shifts for the impurity nuclei Sn[119] (concentration ≈ 1 at.%) as a

FIG 1　　　　　　　　　FIG 2
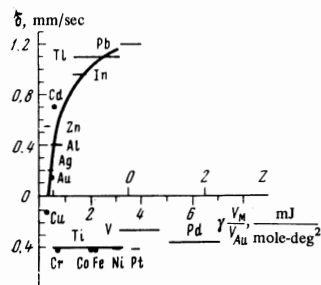
FIG. 1. Dependence of the isomer shift (relative to Mg_2Sn) for Sn[119] impurity nuclei (≈ 1 at. %) in different metals on the value of $\gamma V_M/V_{Sn}$. The values of the shifts are taken from [2,3, 8]. The horizontal segments denote the uncertainties in the measurement of γ.

FIG. 2. Dependences of the isomer shifts for impurity nuclei Au[197] in different metals on the value of $\gamma V_M/V_{Au}$. The values of the shifts are taken from [10].
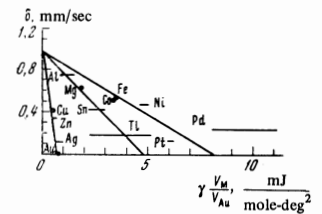
function of the coefficient of the electronic specific heat γ[9] of the matrices, multiplied by the ratio of the atomic volumes of the matrix and tin. If the values of the isomer shift are combined in accordance with the groups of matrices having identical valence, then it can be noted that the plots have different slopes. The slope increases with increasing Z, as expected from the expression for ρ, taking into account the negative sign of U for the case of the Sn impurity (it is usually assumed that Z is proportional to U). Apparently the actual contribution to the isomer shift from the band states is small. The main role is played in this case by the contribution from the local state, which determines the consecutive displacement of the values of the isomer shift upward for groups of matrices with identical valence with decreasing perturbation. The tendency of the dependence for normal metals to saturation in the region of heavy elements is apparently due to the influence of the limiting value of the number of 5f electrons in the impurity cell, which cannot be larger than 2, and to the possible increasing screening due to the 5p-electrons.

The group of transition metals lies separately from the normal metals, and the isomer shifts are small and approximately constant in magnitude. Apparently this is due to the large density of the states in the conduction band of the matrix, leading to an almost complete screening of the impurity in the impurity cell in each transition metal.

The dependences of the isomer shifts for the impurity nuclei Au[197] in metallic matrices on the coefficient of the electronic specific heat (corrected for the change in the atomic volume of the impurity) have a different form than in the case of impurity tin (Fig. 2). It is seen that it is necessary to take into account here only the contribution from the band states, for which, taking into account the positive sign of U, we can expect on the basis for the expression for ρ a decrease in the isomer shift with increasing density of the states of the matrix. We see that the slopes of the plots depend on the difference between the valences V of the impurity and the matrix, and the larger Z the smaller the fraction of the charge attracted by the impurity Au nucleus for the same change in the value of $\gamma V_M/V_{Au}$, as follows from

the expression from the first term of ρ. The absence of a local state is also indicated by the fact that no difference is observed in the variation of the shifts for matrices of normal and transition metals, and also that the dependence of the isomer shift for matrices with different valences converge, accurate to within the error for the data on the coefficients of the electronic specific heat, to approximately one point. This value of the isomer shifts, equal to approximately 1 mm/sec relative to metallic Au, can apparently be regarded as the maximum possible value for impurity Au nuclei and corresponds to filling of two 6s-states.

It is seen from the considered cases of Sn and Au impurities in metallic matrices that the Goodings-Mozer formula explains the tendencies of the dependences of the isomer shifts for these impurity nuclei, if account is taken of the valence difference between the impurity and the matrix, but does not take into account the individual features of the impurity atom. For example, the attracting character of the impurity potential of Au does not follow at all from this formula.

[1] R. Ingalls, Phys. Rev. **155**, 157 (1967); R. Ingalls, H. G. Drickamer, and G. de Pasquali, Phys. Rev. **155**, 165 (1967).

[2] N. N. Delyagin, Fiz. Tverd. Tela **8**, 3426 (1966) [Sov. Phys.-Solid State **8**, 2748 (1967)].

[3] V. A. Bryukhanov, N. N. Delyagin, and V. S. Shpinel', Zh. Eksp. Teor. Fiz. **47**, 2085 (1965) [Sov. Phys.-JETP **20**, 1400 (1965)]. V. V. Chekin and V. G. Naumov, ibid. **50**, 534 (1966) [**23**, 355 (1966)]. F. Pobell, Phys. Stat. Solidi **13**, 509 (1966).

[4] V. V. Chekin and V. G. Naumov, Zh. Eksp. Teor. Fiz. **51**, 1048 (1966) [Sov. Phys.-JETP **24**, 699 (1967)].

[5] I. M. Lifshitz, Usp. Fiz. Nauk **83**, 617 (1964) [Sov. Phys.-Usp. **7**, 549 (1965)]; Zh. Eksp. Teor. Fiz. **53**, 743 (1967) [Sov. Phys.-JETP **26**, 462 (1968)].

[6] D. A. Goodings and B. Mozer, Phys. Rev. **136**, A1093 (1964).

[7] T. B. Massalski and L. L. Isaacs, Phys. Rev. **138**, A139 (1965).

[8] V. A. Bryukhanov, N. N. Delyagin, and V. S. Shpinel', Zh. Eksp. Teor. Fiz. **47**, 80 (1964) [Sov. Phys.-JETP **20**, 55 (1965)]. B. Street and B. Window, Proc. Phys. Soc. **89**, 587 (1966); A. J. F. Boyle, D. St. Bunbury, and S. Edwards, Phys. Rev. Lett. **5**, 553 (1960).

[9] Low Temperature Physics, Springer Encycl. of Physics, 1955. vols. 14–15.

[10] P. H. Barrett, R. W. Grant, M. Kaplan, D. A. Keller, and D. A. Shirley, J. Chem. Phys. **19**, 1035 (1963); L. D. Roberts, R. L. Becker, F. E. Obenshain, and J. O. Thomson, Phys. Rev. **137**, A895 (1965).