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MÖSSBAUER EFFECT ON Sn^{119} IMPURITY NUCLEI IN BINARY METALLIC SOLID SOLUTIONS

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Mössbauer effect probabilities and isomeric shifts were measured for the Sn^{119} γ transition on nuclei incorporated as impurities in Ag-Pd, Ag-Au and Ag-In binary matrices as well as in Ag-Sn alloys. The dependence on the composition of the binary matrix of the electron density at the nucleus and the effective Debye temperature, which characterizes the probability for the effect, were found over a wide range of concentrations. It is shown that both the probability for the effect and the size of the isomeric shift (as well as the width of the absorption line) are extremely sensitive to features of the electron structure of the host; in particular, the dependence found for the hosts containing a transition metal (palladium) is markedly different from that observed for other matrices. A discussion is given of some features of the behavior of other impurity atoms in metal hosts.

INTRODUCTION

THE study of the Mössbauer effect on impurity nuclei greatly extends the scope of the nuclear resonance method for solving problems of solid state physics. The study of the behavior of impurity atoms in metallic systems is of particular interest. Recently data have been obtained[1,2] on the Mössbauer probability and isomer shift of the γ transition in Sn^{119} nuclei incorporated as impurities in various metallic hosts. Comparison of the experimental data on the probability of the effect and its temperature dependence with the theory of the Mössbauer effect on impurity nuclei [3] showed in particular that within the accuracy of the measurements no difference was observed between the effective force constants between the impurity atom and the host atoms and between the host atoms themselves. Measurement of the isomeric shift of the transition for a large number of hosts established[2] the existence of a clear connection between the electron density at the nucleus of the impurity atom and the effective force constant of the host; the force constant is large if the electron density at the impurity tin nucleus is small.

The data show that when an atom (ion) of tin is incorporated into a metallic matrix, its effective charge is changed slightly, as a result of which there is an equalization of the interaction strength with a corresponding change in the electron density at the nucleus of the impurity atom.

More complete data concerning the influence of the electronic structure of metallic systems on the characteristics of the Mössbauer effect could be obtained by studying binary alloys of tin over as wide a range of concentrations as possible. We shall give results of such measurements for Ag-Sn alloys later. But this line of investigation is limited, since tin does not form a continuous range of solid solutions with any one of the metals. A more interesting and promising possibility was also followed in this work: the study of the Mössbauer effect on impurity Sn^{119} nuclei in hosts which are binary solid solutions, permitting variation of concentration over a wide range (for example, the Ag-Pd system). One may hope that the equalization of the force constants for monatomic metallic hosts, which was mentioned above, will also occur for the impurity tin atom in binary systems. In this case the change in the electronic structure of the binary host with composition should be directly reflected in the values of the Mössbauer probability and the isomeric shift.

DESCRIPTION OF THE EXPERIMENT

In the present work we have studied disordered binary alloys of silver with gold, palladium, tin and indium. Silver forms with palladium and gold a continuous sequence of solid solutions; the Sn-Ag system is one of the few systems in which the solubility of tin in the second component exceeds 20%. One of the criteria for the choice of the alloys was a sizable solubility of tin in each of the components.

Samples were prepared by melting appropriate amounts of the components in vacuum. In the alloys of the Ag-Sn system we used normal tin; in the other alloys, in addition to the main components we also introduced a small amount of tin enriched to 66.3% in the Sn^{119} isotope. The alloys were then homogenized by annealing. The absorbers were prepared by rolling the samples into foils of the required thickness; in some cases we used powders obtained by grinding the alloy. After rolling, the samples were again annealed. In the case of binary alloys a quite long anneal is needed if one is to get the right effect. For example, for Ag-Pd alloys, where the isomeric shift is strongly dependent on the composition of the host, the absorption line in insufficiently annealed samples was significantly broadened. The anneal was usually carried out for several tens of hours at temperatures of 500—800° C. The resonance absorption spectra were measured periodically; the anneal was continued until there was no further reduction in the width of the absorption line.

The technique of the measurements and the handling of the data were similar to those used by us earlier.[1,4] The measurements were made at absorber temperatures in the interval from 77 to 290° K. The source was magnesium stannide, Mg_2Sn, containing Sn^{119m}, at a temperature of 77° K. The source parameters were determined earlier.[4] Because of selective absorption by the palladium of the x rays of tin, the use of alloys containing palladium resulted in a slight change (dependent on absorber thickness) in the fraction of resonance radiation in the total flux of quanta. The size of the corresponding corrections (which did not exceed 5%), which had to be made when calculating the magnitude of the effect, were determined by separate measurements using palladium filters of various thicknesses. The probability of the effect f' was determined for the Ag-Pd and Ag-Au alloys over the whole concentration range, and also for the alloy Ag-Sn (24.2% tin). In the other cases the determination of f' was not of particular interest because of the relatively small range of concentrations within which one could make the measurements.

The resonance absorption spectra had a simple shape for all the samples: a single absorption line with a width corresponding to the natural width of the γ line or, in certain cases, somewhat larger than the natural width. For the Ag-Sn alloys with tin content 13.5% and 24.2%, the slight broadening is easily explained by the noncubic structure of the alloys. The other cases of broadening will be considered below. For the Ag-Au and Ag-In alloys, as well as for the alloys Ag-Sn (8% tin) and Ag-Pd with low concentrations of silver and palladium, the width of the absorption line agreed within the limits of error with the natural width of the γ line.

RESULTS AND DISCUSSION

The main results of the measurements are given in the table. For the Ag-Pd and Ag-Au alloys and also for the Ag-Sn alloy (24.2% tin) we determined the absolute value of the effect f' and its temperature dependence. Considering the relatively small temperature interval in which the f' measurements were made and the rather low sensitivity of the Mössbauer probability to details of the phonon spectrum, it is convenient to use a one-parameter description of the values of f' and their temperature dependence in terms of the effective Debye temperature Θ. In all cases there was very good agreement of the experimental values of f' with those calculated on the Debye approximation using the Θ values given in the table.

Figure 1 shows the change in the values obtained for Θ as a function of concentration for the alloys Ag-Au and Ag-Pd. We see that the change in Θ with composition is significantly different for these two systems. The near equality of the force constants for gold and silver results in a

Isomeric shifts δ of the Sn^{119} transition and effective Debye temperatures for an impurity atom of tin in metallic hosts*

Host composition at%	tin impurity at%	σ, mm/sec		Θ, °K
		299°K	77°K	
100 Pd	1.50	—0.41	—0,36	257±8
74.0 Pd — 26.0 Ag	1.60	—0.37	—0.32	250±11
50.0 Pd — 50.0 Ag	1.21	—0,31	—0.26	250±9
25.3 Pd — 74.7 Ag	1.00	—0.17	—0.14	232±10
10.1 Pd — 89.9 Ag	1,28	—0.12	—0.06	225±10
5,0 Pd — 95.0 Ag	1,25	+0,03	+0.06	221±12
100 Ag	1.23	+0.17	+0.20	207±12
24.2 Au — 75,8 Ag	1,02	+0,15	+0.19	210±10
49.5 Au — 50.5 Ag	2,00	+0,12	+0.15	210±12
75.5 Au — 24.5 Ag	0.90	+0.13	+0,15	205±10
100 Au	1.70	+0.12	+0.15	220±10
8.0 Sn — 92.0 Ag	—	+0.21	+0.24	—
13,5 Sn — 86,5 Ag	—	+0,22	+0,26	—
24.2 Sn — 75.8 Ag	—	+0.28	+0.33	196±14
100 Sn	—	—	+0.66	—
8.9 In — 90.1 Ag	2,40	—	+0,25	—
15,0 In — 85.0 Ag	2,90	—	+0,30	—
100 In	1,00	—	+0,98	—

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*The isomeric shifts were measured relative to the energy of the γ transition in Mg_2Sn, which was at 77°K; the shifts were measured to an accuracy of 0.02 mm/sec. The composition of the host does not include the tin impurity.

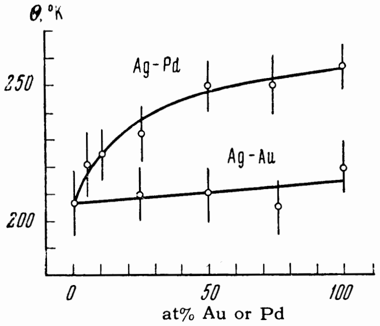

FIG. 1. Dependence of effective Debye temperature Θ for tin impurity atoms in Ag-Pd and Ag-Au alloys on composition of the host.

practically constant Θ over the whole range of concentrations of the Ag-Au alloys, despite the large difference in mass of the silver and gold atoms. In the Ag-Pd system the effective Debye temperature varies smoothly (but not linearly) with change in composition of the host.

Of great importance is the correlation between the effective Debye temperatures and the values of the isomeric shifts, which have a similar behavior for the binary matrices to that[2] found earlier for monatomic metallic matrices. Despite the sizable errors in determining the effective Debye temperatures, a comparison of the dependence on composition of Θ (Fig. 1) and the isomeric shifts δ (Fig. 2) for the Ag-Pd alloys clearly shows the presence of such a correlation. For the Ag-Au alloys both Θ and δ change very little with composition of the host; the values of Θ obtained for the Ag-Sn (24.2% tin) alloy also are not in contradiction with the assumption of a correlation between Θ and δ.

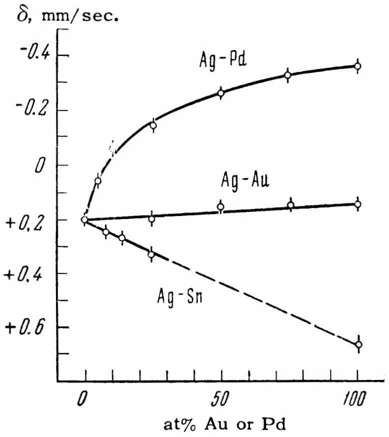

FIG. 2. Dependence on host composition of the isomeric shifts δ for the Sn^{119} γ transition in binary matrices of Ag-Pd, Ag-Au and Ag-Sn. The shifts were measured relative to the energy of the transition in Mg_2Sn with source and absorber temperatures 77°K. A decrease in isomeric shift corresponds to a decrease in the electron density at the Sn^{119} nucleus.

Thus, for binary metallic hosts also one finds a connection between the electron density at the impurity nucleus and the value of the interaction forces where, as in the case of monatomic hosts, a decrease in electron density at the impurity nucleus corresponds to an increase in the force constants. But it would appear to be incorrect to extend to all binary matrices the assumption of complete equalization of interaction forces for all atoms of the system by means of the mechanism of redistribution of electron density which was discovered earlier.[2] In fact, if there were complete equalization of the interaction forces, then regardless of the composition of the host, all the impurity atoms would be completely equivalent, and the absorption line (for crystals with a cubic lattice) would have the natural width. But the lines were broadened for the alloys Ag-Pd (50.0% and 25.3% palladium). The largest broadening (about 0.2 mm/sec) was seen for the alloy containing 50% palladium, i.e., for the composition at which the statistical weights are comparable for the largest number of different configurations of nearest neighbors of the impurity atom. One may therefore conclude that, at least for alloys containing a transition metal (palladium), the interaction strength (and the electron density at the nucleus of the impurity atom) depends on the configuration in the immediate surroundings of the impurity atom.

The dependence of the isomeric shift δ on composition of the hosts is also very typical (Fig. 2). For the Ag-Au alloys the shift changes little with change of composition because the force constants in pure gold and silver are almost equal. In the Ag-Sn system the shift changes linearly with tin concentration where, as shown in Fig. 2, the extrapolation to pure tin agrees well with the experimental value of δ for tin. This additivity also holds approximately for matrices in the Ag-In system (although these alloys, because of the high tin content, should already be regarded as ternary systems). A completely different variation of isomeric shift with composition is observed for the Ag-Pd alloys, where there is a marked deviation from linear dependence. There is already a sizable change in the isomeric shift at low concentrations of palladium. The electron density at the nucleus of the impurity atom rapidly reaches a value close to that in pure palladium, and changes little for large palladium concentrations.

In the simple band theory of electronic structure, palladium is treated as a superposition of d bands, containing 0.6 d-holes per atom, and s bands containing this same number of electrons. The data on magnetic properties of Ag-Pd alloys [5] are explained satisfactorily on the assumption that the s electrons of the silver in the alloy fill the free d levels; this filling is completed at a silver concentration around 60%, after which the alloy becomes diamagnetic. If we assume that the collectivized electrons of the impurity tin atoms fill the levels of the d band equivalently to the s electrons of silver, then it is not difficult to see that the data found for the dependence of isomeric shift on composition of the host cannot be explained within the framework of the simple band model. In fact, according to this model, at low concentrations of palladium the number of free d levels is so small that filling them could not give rise to the marked change in the isomeric shift which is seen experimentally. An alternative interpretation of the data on the basis of some other specific model can hardly be convincing when we consider the lack of sufficient data about the effect on the electron density at the nucleus of various factors (for example, the screening effect of electrons in the d band).

It is interesting to compare the results of this work and earlier papers [1,2] using tin impurities, with the results of similar investigations carried out with other impurity atoms. The results of measurements of the Mössbauer probability and temperature shift for impurity iron atoms in monatomic metallic hosts, [6,7] show that in this case apparently there is an equalization of the interaction forces between the impurity atom and the host and between host atoms. Considering the marked difference in the electron configuration of the tin and iron atoms, one must, however, assume that the details of the mechanism for equalization are essentially different in the two cases. The limited amount of published data on isomeric shifts for the Fe^{57} transition in metallic hosts does not permit us to find the connection between the electron density at the Fe^{57} impurity nuclei and the parameters of the host.

Recently Barrett et al [8] have measured isomeric shifts for the 77 kev transition in Au^{197} incorporated as an impurity in metals. They did not consider the problem of the connection between the electron density at the nucleus of the impurity atom and the dynamical parameters of the host. It is natural to try to treat the data of Barrett et al from this point of view, as was done earlier for tin impurity atoms. [2] It turned out, however, to be impossible to get a unique connection between the electron density at the nucleus of the gold impurity atom with any of the parameters of the hosts that we had treated earlier. [2] This is an indication of a more complicated behavior of the gold impurity atom in metals (as compared to tin atoms). One may suppose, for example, that the d electrons make an important contribution to the interaction for the gold impurity atoms. This may possibly be related to the difficulty in interpreting the results of studies using the Mössbauer effect of the Al-Ni system, for which the simple band model assumes a mechanism of filling of the d levels by the s electrons of the gold, analogous to the mechanism treated above for the filling of the d levels in the Ag-Pd system. Obviously the paucity of available data at the present time prevents a more detailed treatment of the results discussed above. A systematic investigation of the Mössbauer effect on impurity atoms in metallic hosts, especially binary hosts, using different impurity atoms, might give important information about the electronic structure of metallic systems and the nature of the interatomic interaction in such systems.

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