Cluster formations of $FeSn_2$ in white tin single crystals

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The Mössbauer effect on Fe^{57} impurity nuclei is investigated in single-crystal and polycrystalline white tin. Data on the real phonon spectrum of tin are employed to interpret the experimental results. The causes of the sharp difference between the experimental and theoretical dependences of the probability of the effect on temperature and orientation of the crystallographic axes of the sample with respect to direction of the recorded γ-ray beam are discussed. The discrepancy is ascribed to the presence of cluster formations (of the $FeSn_2$ type) in the white-tin matrix.

1. FORMULATION OF PROBLEM

The discovery of the Mössbauer effect has created a research method with which to obtain information directly from the impurity nucleus. The methodological capabilities connected with nuclear γ resonance turned out to be unique both in the variety of the obtained information and in the unusually high sensitivity to those local conditions under which the atom is situated in the crystal lattice.

The principles of a rigorous theory of the dynamic properties of an impurity nucleus in a crystal were established by the papers of I. Lifshitz[1]. The discovery of the Mössbauer effect has stimulated further development of the theory of dynamic properties of a crystal with defects. A fundamentally new circumstance was the possibility of verifying, at last, the conclusions of the rigorous theory in direct experiment. The main emphasis in the theoretical papers on the Mössbauer effect for the impurity nucleus in the crystal was on the main properties of the selected model on which the rigorous calculation was based[2]. It turned out that certain rather natural assumptions make it possible to simplify the problem to such an extent that relations of general character can be reduced to concrete calculation formulas[3].

We note in particular that any deviation of the theoretical relations from those observed in experiment makes it possible in principle to draw conclusions not only on the applicability of the theory to any particular case, but also to assess, in accordance with the character of the discrepancy, the peculiarities of the behavior of the investigated nucleus.

The purpose of the present paper was to investigate the Mössbauer spectra of Fe^{57} nuclei contained as cluster formations in the crystal lattice of white tin, on the basis of results obtained by comparing the experimental relations with the theoretical ones.

The choice of the object was dictated by the following considerations:

1. In view of the negligibly small solubility of iron in white tin[4], we can expect beforehand appreciable discrepancies between experiment and a theory based on the assumption that the impurity has a sufficiently good solubility in the host. From the character of these discrepancies one could ascertain, by means of a concrete experiment, the methodological suitability of Mössbauer spectroscopy to the investigation of cluster formations.

2. In the case of iron impurity nuclei in β-Sn, the usual uncertainty connected with the absence of sufficiently exact data on the real phonon spectrum of the matrix is eliminated. By now, this spectrum has been sufficiently well investigated for β-Sn crystals[5, 6], so that a comparison of the experimental relations with the theoretical ones is of considerable interest.

3. In the overwhelming majority of experimental studies of the dynamic properties of impurity nuclei by the Mössbauer effect, the impurity was introduced into a polycrystalline sample. Yet it is possible to employ the methodological capabilities of the Mössbauer spectroscopy also to a fuller degree by introducing the impurity nuclei into a single crystal. The white-tin matrix is essentially anisotropic (space group D_{4h}^{19}), and anisotropy of the Mössbauer-effect probability was observed earlier on Sn^{119} nuclei in the β-Sn lattice[7–9].

2. Fe^{57} IN β-Sn

A tin sample with the introduced iron impurity was used as the radiation source. The nuclei of the parent isotope Co^{57} were deposited on the surface of the tin sample by electrolysis from a $CoCl_2$ solution without a carrier, and were introduced into the sample by diffusion (at a temperature 5–6° below the melting point of tin for 6 hours in an atmosphere of hydrogen).

During the course of preparation of the investigated samples, it was verified that the Co^{57} nuclei were indeed introduced into the β-Sn as a result of annealing. To this end, we measured the intensity of the emission of a tin foil, on one of the surfaces of which Co^{57} nuclei were deposited. A comparison of the emission intensity of the sample with the "active" side and the opposite side, carried out before and after the annealing, has established that the effective depth of penetration of the Co^{57} nuclei in β-Sn is approximately 2μ.

The experiments on the Mössbauer effects were carried out with polycrystalline and single-crystal tin samples having activity $\sim 5\ \mu$Ci (the samples were prepared by the same technology). The absorber was a stainless-steel foil 12.3 μ thick (at room temperature in all the experiments).

For the Fe^{57} nuclei in the polycrystalline β-Sn sample at room temperature, the Mössbauer spectrum consists of a single line (Fig. 1). The line width is 0.61 ± 0.02 mm/sec. The temperature measurements have revealed no noticeable change in the width and shape of the line and the line itself was symmetrical within the limits of experimental errors. The spectra for the polycrystalline and single-crystal samples were the same.

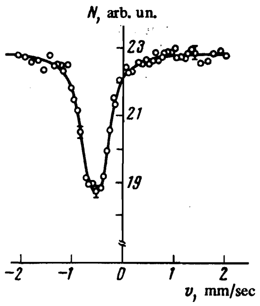

FIG. 1

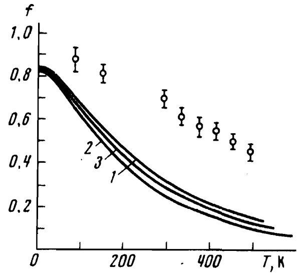

FIG. 2

FIG. 1. Mössbauer spectrum of Fe^{57} in β-Sn at room temperature. The absorber is stainless steel.

FIG. 2. Temperature dependence of the probability of the Mössbauer effect for Fe^{57} nuclei in β-Sn. The solid curves show the theoretical plots for the directions [100] (1) and [001] (2) in the single crystal, and also the polycrystal (3).

The fact that the investigated samples were used as a radiation source has made it possible to simplify to the utmost the reduction of the obtained Mössbauer spectra. To determine the probability of the effect we chose, in particular, the area method [10]. The advantage of this method over others is that in the absence of resonant absorption in the source the area of the spectrum is proportional to the probability of the effect, and for the emitting nuclei it is independent of the shape of the resonance curve (and is independent also of parasitic vibrations of the setup). The standard sample was in this case a source in the form of a stainless-steel foil 3 μ thick with uniformly distributed nuclei Co^{57}. The probability of the effect for such a sample was determined earlier in [11].

Figure 2 shows the temperature dependence of the probability of the Mössbauer effect for Fe^{57} nuclei in polycrystalline β-Sn. Attention is called to the large probability of the effect at low temperatures and to its relatively weak decrease with increasing T. Thus, at liquid-nitrogen temperature, the probability of the effect is 0.87 ± 0.06, and at room temperature it is 0.87 ± 0.03. We note that the experimental error in the determination of f, shown in the figure, includes also a systematic error. Therefore the character of the f(T) dependence was actually determined somewhat more accurately than the absolute value of the probability, as can be seen from the scatter of the points.

An attempt to observe anisotropy of the probability of the effect for Fe^{57} nuclei in β-Sn was undertaken in experiments with two single crystals having different orientations. The normal to the surface of one of the crystals coincided with the [001] direction, and for the other with the [100] direction (accurate to 1°). For both samples we determined the probability f of the effect as a function of the angle φ between the directions of emission of the registered γ quanta and the normal to the sample surface. The sample was rotated in this case about the [010] axis. The distance from the radiation detector to the sample was chosen to be large enough to ensure a negligibly small beam divergence. The measurements were performed at room temperature.

In the reduction of the results of these measurements, a correction was introduced for the background due to the harder lines (mainly from the strong x-rays of the K line of tin). The value of the background was determined with the aid of a set of copper and aluminum absorbers for each of the chosen values of the angle φ.

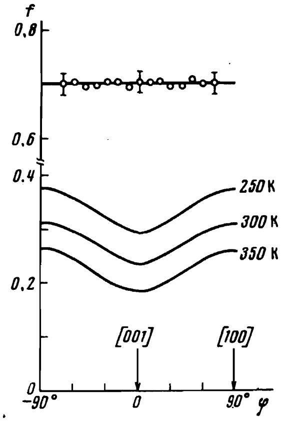

FIG. 3. Concerning the anisotropy of the probability of the Mössbauer effect for Fe^{57} nuclei in β-Sn. The experimental points were obtained at room temperature. The solid lines correspond to the data obtained from the theoretical calculations.

Within the limits of experimental error, we observed no dependence of the probability of the effect on the orientation of the sample relative to the direction of the registered beam of γ quanta (Fig. 3). The probability of the effect turned out to be 0.70 ± 0.02.

After the termination of the experiments, an x-ray structure analysis was performed for that sample for which the data on the Mössbauer effect are shown in Fig. 3. It was established that the sample surface through which the radioactive Co^{57} nuclei were introduced is single-crystal (with a block angle less than 1′).

The shift of the Mössbauer line of the Fe^{57} nuclei in β-Sn relative to the line for stainless steel was 0.59 ± 0.02 mm/sec at room temperature.

3. PROOF OF THE EXISTENCE OF CLUSTERS

To obtain the theoretical dependences of the Mössbauer-effect probability on the temperature and on the γ-quantum emission direction, we made use of the results of [3] for an impurity nucleus and an arbitrary polyatomic regular crystal.

The results of such calculations are meaningful under the following basic assumptions: 1) the impurity nucleus is located at a crystal-lattice site; 2) the force constants for this nucleus are the same as for the matrix nuclei ("isotopic" impurity); 3) the vibrations of the nuclei are harmonic. All the calculations were carried out with a computer, with account taken of the data on the real phonon spectrum of white tin [5].

The intensity of the Mössbauer line for an impurity nucleus of mass m′, in a crystal consisting of nuclei with mass m, is determined by the Lamb-Mössbauer factor

$$f_t = \exp(-2W_t),$$

where the argument of the exponential $2W_t$ is a functional of the spectral density of the square of the displacement of the impurity atom $G_t^\nu(\omega)$ along the principal axes, expressed in terms of the spectral density $g_t^\nu(\omega)$ of the matrix atoms (t and ν are indices that number the places in the unit cell and the principal crystallographic directions) [3].

Inasmuch as $m' < m_t$ in our case, one must allow for the possible existence of discrete frequencies in the vibrational spectrum of the impurity nucleus. We have therefore undertaken first to determine the discrete frequencies ω^ν. This has made it possible to establish that for each of the principal directions in the crystal there is indeed a discrete frequency (which is "free"). Taking this circumstance into account, we obtained the function G_t^ν for the directions [100] and [001]. It turned out that the discrete frequencies constitute an appreciable fraction of the spectrum: the contribution of the δ function to the total area under the $G^\nu(\omega)$ curve is 0.68 and 0.42 for the directions [100] and [001], respectively. In addition, the discrete frequency $\omega^{[100]}$ lies higher on the frequency axis than $\omega^{[001]}$ (1.07 and 1.03, respectively). Accordingly, we have $f^{[100]} > f^{[001]}$ everywhere up to temperatures close to the melting point of tin (Fig. 2). In the limiting case $T \approx 0°K$ we have $f^{[100]} = 0.84$ and $f^{[001]} = 0.83$.

The probability of the effect, in accordance with calculations within the framework of the chosen model, increases like $\exp(a \sin^2\varphi)$ on going from the direction [001] to [100] (or to any other direction in the (001) plane), as is seen from Fig. 3. According to the same data, the anisotropy of the probability of the effect, a measure of which can be the quantity $(f^{[100]} - f^{[001]})/f^{[100]}$, increases similarly with increasing temperature and reaches, for example at room temperature, 25%. Just as in the case of Sn^{119} nuclei in β-Sn[5,9], at low temperatures one can note that the anisotropy of the probability tends to zero may possibly also reverse sign.

As expected, a comparison of the experimental data with the calculated ones reveals a sharp discrepancy between them (Figs. 2 and 3). The theoretical calculation predicts anisotropy of the probability of the effect, observation of which in experiment entails no particular difficulty. On the other hand, the results of the experimental research show that the anisotropy of the probability is not observed within the limits of the measurement accuracy (4% of f). There are strong differences between the absolute values of the probability of the effect (by more than a factor of 2 at room temperature). There is even no qualitative agreement between the f(T) relations: the calculated value of the probability decreases with increasing temperature much more rapidly than would follow from the experimental data.

The relatively large probability of the effect is evidence of rather strong chemical bonds between the iron atom and its nearest neighbors.

To determine the influence of the change of the force constants, we have attempted to establish the "possibilities" of obtaining the probability of the effect on the basis of the experimentally known phonon spectrum of β-Sn, by varying only the force constants of the iron impurity nucleus at the lattice site. To estimate the probabilities, we used the formulas obtained in[12] for an impurity nucleus in a cubic crystal, with allowance for the change of the force constants of the central interaction with the nearest neighbors.

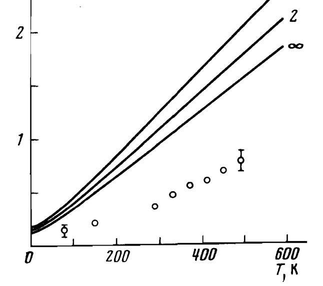

FIG. 4. Temperature dependence of the argument of the exponential in the Lamb-Mössbauer factor for Fe^{57} nuclei in β-Sn. The theoretical curves were calculated for different ratios λ of the force constants of the interaction with the nearest neighbors of the iron nuclei and the tin nuclei in β-Sn.

A change of the force constants by a large factor is not very likely. Therefore, at large limits of these changes, one can attempt to treat all other unaccounted-for factors (noncentral interaction, neighbors from the next coordination spheres, the character of the lattice symmetry, which in this case is tetragonal and not cubic) as a change of the force constants of the central interaction with the first coordination sphere. It turned out that the "possibilities" of the force constants are limited: assuming them to be free parameters in the equations, it is impossible to obtain agreement between the theoretical and experimental dependences by a suitable choice of these constants (Fig. 4).

Thus, the phonon spectrum of the iron atom turns out in the real case to be such that it coincides with not even one of the possible spectra of this atom when it occupies "simply" the place of the tin atom in the lattice site. In view of the not-too-large difference between the atomic radii of Fe and Sn, and with allowance for the relatively close packing of the β-Sn lattice, we must reject the assumption that the iron atom is in an interstice.[13]

The foregoing results of the comparison of the calculated and experimental data prove that the form of the Fe is present in Sn at small Fe concentrations not as a dissolved impurity, but as cluster formations of an intermetallic phase.

Among the known chemical components which are typical of the Fe-Sn system[4], the closest to β-Sn in the character of the lattice symmetry is $FeSn_2$. It is precisely this compound which forms, together with β-Sn, a heterogeneous region of the phase diagram at low iron concentrations in tin. One can hardly regard it as an accident that the shift of the Mössbauer line of Fe^{57} nuclei in β-Sn is approximately the same as for $FeSn_2$[14]. In view of these circumstances, we have carried out thorough investigations of the temperature dependence of the shift δ and of the probability f of the Mössbauer line of Fe^{57} nuclei in $FeSn_2$.

4. Fe^{57} IN $FeSn_2$

To investigate the temperature dependence of the Mössbauer-spectrum parameters of the Fe^{57} nuclei in $FeSn_2$ we used the samples described in[14]. In view of the fact that the $FeSn_2$ compound is antiferromagnetic (with $T_N = 380°K$[15]), particular attention was paid to introduction of a correction for the "saturation effect," the side effect of which in the determination of the f(T)

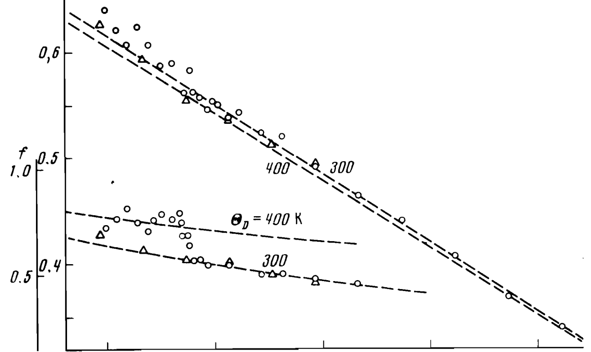

FIG. 5. Temperature dependence of the shift δ (relative to the line in Cr) and the factor f of the Mössbauer line of Fe^{57} nuclei in β-Sn (△) and in $FeSn_2$ (○). The dashed curves correspond to the Debye approximation.

dependence is, as is well known, the most significant in the region of the magnetic transformation. The results are shown in Fig. 5 together with the data for the Fe^{57} nuclei in β-Sn.

As seen from the figure, at $T > T_N$ the f(T) dependence for $FeSn_2$ coincides within the limits of experimental errors with the analogous dependence for β-Sn. On the other hand, in the region $T < T_N$ there are large discrepancies between these dependences. The data for β-Sn are described sufficiently well within the framework of the one-parameter approximation at $\Theta_D \approx 300°K$ in the entire compared temperature interval, whereas in the case of $FeSn_2$ one observes an appreciable increase of the effective Debye temperature on going into the region of existence of magnetic order. This discrepancy can be naturally connected with the "magnetic anomaly" of the Lamb-Mössbauer factor in magnetic transformations, an anomaly due to the dependence of the energy on the interatomic distances[16,17].

As to the $\delta(T)$ dependences, they are in quite good agreement (Fig. 5). This result can be easily explained by taking into account the fact that the magnetic anomaly of the relativistic correction to the isomer shift of the Mössbauer line at temperatures $T \geq \Theta_D$ is much less sensitive to the crystal phonon-spectrum change due to the magnetic transformation[17]. As a rule, the "magnetic anomaly" of the isomer shift proper (due to striction) is more significant. It appears that this mechanism can explain certain discrepancies between the $\delta(T)$ dependences for $FeSn_2$ and β-Sn at $T \approx 300°K$.

5. CONCLUSIONS

The data obtained in the present investigation show thus that clusters of the $FeSn_2$ type are produced in the β-Sn lattice as a result of diffusion of the iron atoms. The characteristic linear dimension r of these clusters should not exceed several dozen angstroms, inasmuch as a "paramagnetic" line is observed at $T < T_N$ (Fig. 1). On the other hand, the absence of a "magnetic anomaly" in the f(T) dependence for the Fe^{57} nuclei in β-Sn, in contrast to $FeSn_2$ (Fig. 5), gives grounds for assuming that r is of the order of the dimensions of the unit cell.

Since no anisotropy of the probability of the effect is observed (Fig. 3), even though we have $c/a = 0.815$ for $FeSn_2$, the crystal axes of the clusters should be oriented randomly relative to the axes of the β-Sn single crystal, which is strongly anisotropic in its dynamic properties. This can take place if the diffusion of the iron atoms occurs on the boundaries between the grains of the β-Sn crystal.

We note that we have referred above almost throughout to iron atoms in tin, whereas cobalt atoms were introduced into the lattice by diffusion. Experiments on the Mössbauer effect yield information from those places which are occupied by the iron nuclei in the isomer state. These are at the same time the places that are characteristic in the ratio of the dynamic properties for both the iron nuclei and the cobalt nuclei in the tin matrix, since the electron configurations and the masses of the Fe and Co atoms are close to each other. This similarity is reflected, incidentally, in the similarity of the phase diagrams of the systems Fe-Sn and Co-Sn.

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