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NUCLEAR GAMMA RESONANCE IN HIGHLY DISPERSED TIN

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The Mössbauer effect is investigated in highly dispersed tin particles having diameters of 250, 370, 600, and 1550 Å. It is shown that the probability of the effect diminishes as the particle diameter decreases and that this result is associated with the influence of the surface. The Debye temperature Θ is determined for the different groups of particles (120°, 130°, 135°, and 140°K, respectively) and for tin atoms in the surface layer, which had a thickness of five lattice constants (100°K).

HIGHLY dispersed tin was produced by evaporating liquid drops in a helium or argon atmosphere; the vapor condensed afterwards into aerosol particles.[1] When the inert gas was passed through an evaporator the tin particles were trapped on a filter. The particle size was regulated by the rate of flow and also depended on the gas. Under otherwise equal conditions the tin particles were smaller in helium than in argon.

A special technique was employed to prevent oxidation of the tin particles in air. The evaporator was connected hermetically to a glass ampoule with a metal can containing a filter. The ampoule was weighed carefully before the evaporation process started. After a sufficient amount of tin had been shaken into the ampoule the latter was sealed and reweighed to determine the precise amount of tin. This was necessary in order to determine the probability f′ of the Mössbauer effect. The ampoule was then opened in a box that had been purged by a flow of argon for six hours; the tin was poured into another vessel and mixed uniformly with liquid paraffin without being in contact with air. The nuclear γ resonance spectra indicated a practically complete absence of oxidation.[2]

The mean particle size was determined by means of an electron microscope; photographs were analyzed and differential distributions were plotted. The tin was divided into four sets of particles having respective mean diameters of 250, 370, 600, and 1550 Å.

The spectrum for the highly dispersed tin consisted of a single line that is characteristic of ordinary polycrystalline β-Sn with a chemical shift (relative to SnO_2) $\delta E_I = 2.6$ mm/sec. However, the probability f′ of the Mössbauer effect for tin particles with diameters of 250, 370, and 600 Å was smaller than for a β-Sn foil.

We investigated f′ as a function $f' = F(T, d)$ of temperature and particle diameter. Values of f′ were determined from the area under the absorption curve[3] for the internal conversion coefficient $\alpha = 6.3$ and the width $\Gamma = 2.4 \times 10^{-8}$ eV of the excited Sn^{119m} level.

The function F(T, d) is plotted in Fig. 1, where it can be seen that f′ diminishes as the particle diameter decreases, beginning with d = 600 Å; the temperature dependence is steeper. Our results for f′(T) in the cases of the foil and the dispersed tin with the largest (1550 Å) particle diameter agree with the literature.[4-7] An x-ray analysis revealed no difference between the lattice constants

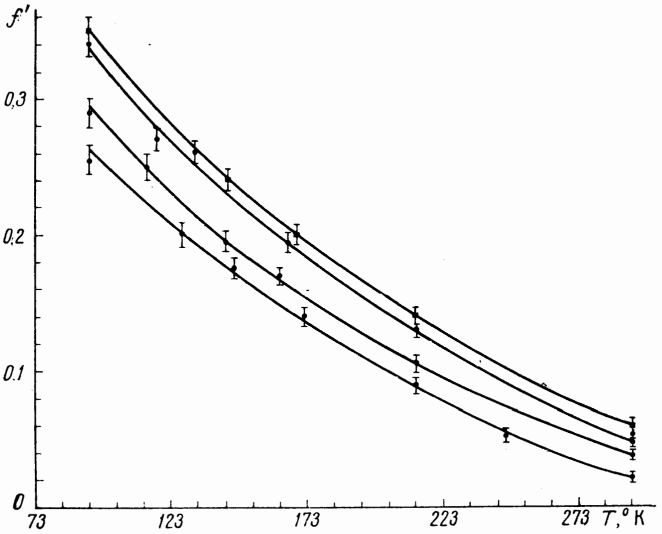

FIG. 1. Probability f′ = F(T,d) of nuclear γ resonance. The uppermost curve represents metal foil and highly dispersed tin with d = 1550 Å. The successively lower curves represent d = 600, 370, and 250 Å.

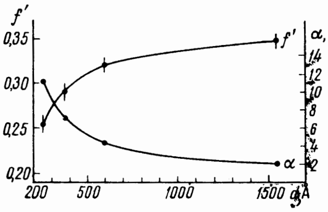

FIG. 2. Dependences of f′ and the specific surface α on the particle diameter d.

T, °K	d, Å	f'_{theor}	f'_{exp}
93	250	0,3	0,254±0,012
93	foil	—	0,350±0,015
300	250	0,045	0,022±0,001
300	foil	—	0,060±0,002

of the dispersed tin and the β-Sn foil; thus ordinary conditions prevailed for the atoms inside the particles. No change of the melting point was observed in the dispersed tin; this indicates an unchanged Debye temperature for the internal atoms.[8] It is therefore reasonable to assume that the diminution of f′ accompanying smaller particles and its stronger temperature dependence are associated with surface phenomena and not with any frequency change in the internal-atom spectra for these particles such as was reported in [9] for highly dispersed gold (but with much smaller diameters ~60 Å).

Figure 2 shows the decrease of f′ at 93°K accompanying the decrease of particle diameter, and also the growth of the specific surface α. We find $f' - f'_\infty \propto -1/d$ (f'_∞ is the probability of γ resonance in the β-Sn foil, and d is the particle diameter) and $\alpha \propto 1/d$, so that f′ and α obey the same law (except for the sign). This indicates that there is a direct relationship between the decrease of f′ and the increase of the specific surface. Certain theoretical calculations also indicate a relationship between the surface effect and the decrease of f′ in highly dispersed tin. Assuming that the variation of f′ is contributed to only by tin atoms in a surface layer having a thickness equal to five lattice constants, f'_{theor} can be calculated from the models in [10,11].

The theoretical and experimental values of f′ are compared in the accompanying table. The experimental values of f′ for surface atoms vary much more rapidly than the theoretical model results.

The Debye temperature was calculated for particles having different diameters and for five different surface layers. The value $\Theta = 140$°K was obtained for β-Sn foil and for high dispersed tin in 1550-Å particles, in agreement with data in [12,13]. Also, for d = 600 Å, $\Theta = 135$°K; for d = 370 Å, $\Theta = 130$°K; for d = 250 Å, $\Theta = 120$°K. For the five surface layers we obtain $\Theta \sim 100$°K. The forces acting on the surface atoms of β-Sn are weakened; this increases the rms spacing of the atoms and decreases f′. Consequently the spectrum of surface β-Sn atoms is here shifted toward lower frequencies than for ordinary β-Sn; for atoms inside the particles there appears to be no change of frequency.

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