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Abstract

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PHYSICS

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DISTRIBUTION OF ELECTRON DENSITY IN GRAY TIN AND DIAMAGNETIC SUSCEPTIBILITY

Among the semiconductor elements of the fourth group of Mendeleev' s periodic system that have a diamond-type crystal lattice, gray tin occupies an extreme position, possessing the smallest forbidden-band width, the lowest value of the characteristic temperature, and the lowest melting temperature. At the same time, tin has high values of the boiling temperature and of the sublimation and evaporation energies. The diamagnetic susceptibility of gray tin is the largest among the semiconductor elements of the fourth group.

It should be noted that researchers have paid considerable attention to the semiconductor properties of gray tin ([1,2]). The entire complex of properties of gray tin and its position in the periodic system account for the considerable interest in the problem of quantitatively studying the distribution of electron density in it.

Experimentally, the study of the distribution of electron density in gray tin is a comparatively difficult task, since the temperature of the polymorphic transformation lies somewhat below room temperature, tin belongs to the heavy elements, and it has a comparatively low characteristic temperature.

The aim of the present investigation was the experimental determination of the atomic scattering factor f of gray tin at room and low (-100°) temperatures and the calculation, on the basis of the experimental values obtained, of f-curves of the electron-density distribution in the crystal lattice at these temperatures.

The object of the investigation was gray tin obtained by recrystallization of white tin into gray tin at a temperature of $-10 \div -20^{\circ}$. The white tin used was of a high degree of purity*. For the photography, a powder of gray tin was used, obtained by grinding in an agate mortar with continuous cooling by dry ice. The powder was then sifted through a fine sieve.

The photography was carried out with CuK_{α} radiation on a URS 50I apparatus

Fig. 1

Figure 1: Fig. 1

with a Geiger-Müller counter. A nickel filter in the form of foil 20μ thick was placed in front of the counter. Cooling of the specimen was carried out by blowing it with nitrogen vapors, the flow rate of which was regulated by means of a heater placed in a Dewar vessel with liquid nitrogen. Temperature control was performed with a copper-constantan thermocouple and an M1198/3 millivoltmeter, with an accuracy of up to 2°.

The intensities of the X-ray reflections were determined from the areas of the peaks recorded on an EPP-09 diagram tape by planimetry.

In calculating the atomic scattering factor, as usual, there were introduced

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* The purification was carried out in the laboratory of N. L. Pokrovskii.

the dispersion correction. Extinction was not taken into account, since a sufficiently fine powder with grain size 5–8 μ was used.

Figure 1 gives the values of the atomic scattering factor as a function of the sum of the squares of the indices, (hkl), of the reflecting planes for room temperature and for a temperature of −100°. Figure 2 gives their logarithms. As is seen from the curves shown, for reflections for which the sum of the squares of the indices exceeds 16, the experimental values of the logarithms of the f-curves lie well on straight lines and, consequently, in this region can be described by a Gaussian function. From the given values of the atomic scattering factors, using the method adopted by us ([3]), the electron-density distribution $\rho = \rho_1 + \rho_2$ in the (110) plane of the crystal lattice of gray tin was calculated. The parameters characterizing the distribution

$$\rho_1 = Ae^{-\alpha r^2},$$

were determined from the linear portion of the logarithm of the f-curve ([4]). For room temperature $A = 406.31$, $\alpha = 15.708$, and for a temperature of 100°, $A = 571.98$, $\alpha = 19.637$. The distribution ρ_2 was determined by summing a three-dimensional Fourier series over the values f_2 ([3]).

Fig. 1. Change in the atomic scattering factor of gray tin at temperatures 20° (a) and −100° (b) as a function of $\sum_i^3 h_i^2$.

Figure 3 shows the calculated electron-density distribution for the directions [111] and [113] at room temperature and at a temperature of −100°. Lowering the temperature is accompanied by an increase in the magnitude of the maxima

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

at the atomic coordinates and by an increase of the maximum at the position 5/8, 5/8, 5/8.

Fig. 2. Change in the logarithm of the atomic scattering factor of gray tin at temperature 20° (a), −100° (b), as a function of

$$\sum_{i}^{3} h_i^2.$$

Figure 4 gives maps of the electron-density distribution in the lattice of gray tin in the (110) plane at room temperature (a) and at a temperature of −100° (b).

In analyzing the data obtained, the following features of the electron distribution in gray tin at room and low temperatures attract attention.

Fig. 3. Distribution of electron density in the directions [111] and [113] in the (110) plane of the unit cell of gray tin at 20° (*a*) and at −100° (*b*).

As in diamond, silicon, and germanium ([4,5]), in gray tin in the [111] direction between the nearest atoms with coordinates 000 and 1/4, 1/4, 1/4 there exists an electronic "bridge" with an electron density of 0.37 el/Å^3. Changing the temperature from room temperature to −100° has practically no effect on the magnitude of this bridge. At the positions 1/2, 1/2, 1/2 and 3/4, 3/4, 3/4, minima of electron density are observed; their value at room temperature is about 0.05 el/Å^3, and at −100° decreases practically to zero. Lowering the temperature is accompanied by an increase in the difference in electron densities at places with small and large values: maxima become higher, and minima lower.

From the electron-density distribution data, some conclusions can be drawn about ionic sizes:

Electron-density level, el/Å^3	1.5	0.25	0.05
Ionic radius Sn, Å	0.75	1.40	2.80

It should be noted that at these same electron-density levels the ionic radii of carbon, silicon, and germanium will be, respectively,

Electron-density level, el/Å^3	1.5	0.25	0.05

Ionic radius C, Å	0.20–0.25	0.95	1.25
Ionic radius Si, Å	0.40–0.47	1.02	1.41–1.50
Ionic radius Ge, Å	0.50–0.57	1.22	1.96–2.00

From the electron-density distribution data, the values of the diamagnetic susceptibility per gram-atom were calculated by the calculation method described earlier ([6]). In this calculation, for a stationary atom the diamagnetic susceptibility of gray tin was found to be $\chi = 38 \cdot 10^{-6}$. It should be noted that, according to the experimental data of Busch ([7]), $\chi = 31.5 \cdot 10^{-6}$; according to his theoretical calculations, $\chi = 38.2 \cdot 10^{-6}$. According to Davden's data ([8]), the experimental value of the diamagnetic susceptibility of gray tin is $\chi = 37 \cdot 10^{-6}$.

These quantities are in satisfactory agreement with the value obtained by us. However, the question of the diamagnetic susceptibility of gray tin from experimental data on electron-density distributions requires further consideration.

Fig. 4. Map of the electron-density distribution in the (110) plane of the unit cell of gray tin at 20° (*a*) and at −100° (*b*)

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Fig. 4. Electron-density distribution map in the (110) plane of the unit cell of gray tin at 20° (a) and at −100° (b)

Figure 4: Fig. 4. Electron-density distribution map in the (110) plane of the unit cell of gray tin at 20° (a) and at −100° (b)

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Note: Figure translations are in progress. See original paper for figures.