“Compression” of the electron shell of a neutral atom by a crystal matrix

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The electron state of impurity tin atoms in the Ga_2Te_3 crystal matrix has been investigated by the nuclear γ resonance method (Mössbauer spectroscopy). It was shown that the impurity tin atoms in loose Ga_2Te_3-type structures were in nonionized atomic states and the compression of their electron shells in the crystal lattice led to a substantial increase in the charge density around Sn^{119} nuclei. A simple quantum-mechanical model has been developed and takes into account the change in s-electron density in an atom placed in a spherical cavity with infinite potential walls. This model can be used to determine the crystal-chemical radii of interstitial impurity atoms, using only data on the Mössbauer isomeric shift. The radius of the impurity tin atom in a Ga_2Te_3-type matrix is estimated.

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This paper reports an investigation of the nuclear γ resonance effect (Mössbauer effect) in the case of interstitial tin nuclei in the Ga_2Te_3 crystal matrix. The lattice of this type of compound (In_2Te_3, Ga_2Te_3) is a very loose crystal structure, and all these compounds have the diamond lattice with tetrahedral coordination of atoms and sp^3 hybrid bonds. In this respect, In_2Te_3 and Ga_2Te_3 are similar to all other diamond-type crystals (Ge, Si, CdTe, ZnS, InSb, GaAs, etc.). In contrast to the latter, however, one-third of the sites of the cation sublattice of In_2Te_3, Ga_2Te_3, and Ga_2Se_3 is unfilled.

It was shown in[1-3], both theoretically and experimentally (using the results on solubility thermodynamics of different impurities in In_2Te_3 and Ge_2Te_3, and data on the electronic properties of doped crystals), that impurity atoms were localized in such loose structures in equilibrium states in the voids of the cation sublattice, remaining in the nonionized, i.e., atomic state. Mössbauer spectroscopy of Sn^{119} impurity nuclei in In_2Te_3 was used in[4] to establish directly that the tin atoms in this matrix were neutral. The neutrality of an impurity atom in crystals whose components are chemically active elements appears to be a unique feature. In semiconducting and dielectric crystals, impurity atoms are usually chemically bonded to the atoms in the matrix.

The aim of the present research was to investigate the electronic state of a tin impurity in Ga_2Te_3 crystals, and to elucidate the effect of the crystal matrix on the s-electron density $\psi_s^2(0)$ around the nuclei.

EXPERIMENTAL RESULTS

The $Ga_2Te_3Sn_x$ specimens were prepared by the method described in[5]. The limiting solubility of tin in Ga_2Te_3 at 630 °C (750-h annealing) was determined by microstructural and x-ray methods, and by measuring the isothermal electrical conductivities. It was found to be 11 at.% ($Ga_2Te_3Sn_{0.11}$). Measurements of the electrical conductivity at room temperature showed that the concentration of charge carriers in single-phase alloys was practically independent of the tin concentration (just as in the case of other impurities in In_2Te_3 and Ga_2Te_3),[3] and the conductivity was intrinsic.

The Mössbauer effect was investigated at temperatures in the range 80–290 °K, using polycrystalline Ga_2Te_3 with different concentrations of Sn^{119} impurity (the enrichment factor was 85%). The absorption spectra of $Ga_2Te_3Sn_x$ ($x \leq 0.11$) consisted of single lines (Fig. 1) with an isomeric shift relative to $BaSnO_3$ of $\delta = +3.69 \pm 0.05$ mm/sec at 80 °K and $\delta = +3.56 \pm 0.05$ mm/sec at 290 °K, which coincided to within experimental error with isomeric shifts for tin nuclei in In_2Te_3.[4] It was shown in[4] that this result was in strict correspondence with the isomeric chemical shift for the neutral tin atom which, in turn, was in complete agreement with theoretical predictions[1,2] on the solubility of impurities in crystals with loose crystal lattices. It is important to note that, when powder specimens of $Ga_2Te_3Sn_x$ were kept in air for a considerable time (~2 months), their Mössbauer spectra showed the presence of an additional line (in fact, a doublet with a small quadrupole splitting and zero isomeric shift). This was undoubtedly due to the formation of complexes involving tin and oxygen.

DISCUSSION OF RESULTS

If the impurity atom forms a chemical bond with atoms in the matrix, the electron density around the nucleus is determined by two factors. On the one hand, we have the redistribution of electrons within the bonds between the given atom and its neighbors and, on the other hand,

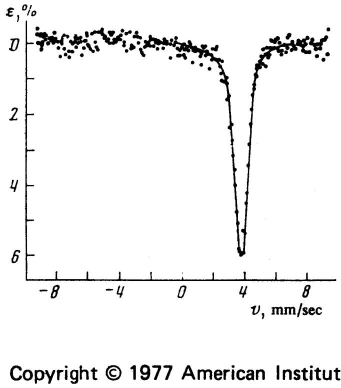

FIG. 1. Absorption spectrum of $Ga_2Te_3Sn^{119}_{0.08}$ (50 mg/cm^2) at 80 °K ($BaSnO_3$ source at 290 °K).

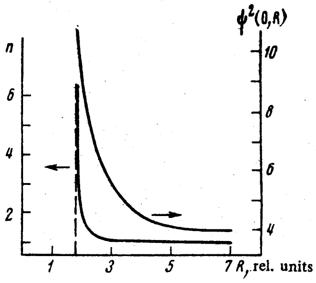

FIG. 2. Principal quantum number n of the ground state of an s electron and the electron density $\psi^2(0)$ as functions of the radius R of an impurity atom in a crystal lattice.

there is the effect of the compression of the electron shell by the surrounding atoms of the matrix. Mössbauer spectroscopy of a neutral atom that does not enter into a chemical bond with the atoms in the crystal matrix can be used to determine in a pure form the influence of compression by the crystal lattice on the electron density distribution.

It is well known[6] that an impurity atom introduced into the crystal matrix tends to push out the lattice atoms, whereas the matrix reacts by compressing the atom so that its crystal-chemical radius R differs somewhat from the free radius. If the impurity atom is not ionized, and does not enter into a chemical bond with the lattice, we may suppose that the wave function for its valence electrons becomes zero at the distance R, where R is the radius of the atom in the matrix.

Let us consider a hydrogen-like atom of nuclear charge Z^* and two electrons in a spherical potential well with infinite walls. The quantity Z^* is the effective Slater charge on the nucleus, including the screening effect due to all the electrons in the inner shells. It will be assumed that the compression of the atom does not deform these shells. In terms of the spherical polar coordinates, the Hamiltonian for an electron is

$$H=-\frac{1}{2}\frac{d^2}{dr^2}-\frac{1}{r}\frac{d}{dr}-U(r), \tag{1}$$

where

$$U(r)=\begin{cases}-1/r & r<R\\ \infty & r>R\end{cases}.$$

The energy and radius R in these expressions are expressed in atomic units ($mZ^{*2}e^2/\hbar^2$ and $\hbar^2/mZ^*e$, respectively).

We shall now determine the energy eigenvalues E and the eigenfunctions $\psi(r)$ of this Hamiltonian for s electrons (orbital angular momentum $l=0$) subject to the condition that $\psi(r)$ must be finite at the origin $r=0$. The solutions are analogous to those for a free hydrogen atom:

$$E=-1/2n^2, \tag{2}$$

$$\psi(r)=A\varphi(r), \tag{3}$$

where $\varphi(r)=e^{-r/n}F$, $F=F(-n+1,\ 2,\ 2r/n)$ is the confluent hypergeometric function, and n is the principal quantum number. The boundary condition $\psi(R)=0$ then yields the following equation for the quantum number n:

$$F(-n+1,\ 2,\ 2R/n)=0. \tag{4}$$

Figure 2 shows the function $n(R)$ obtained by numerical solution of (4) on a computer. As expected, the value of n corresponding to the lowest energy state of the electrons in the atom tends to unity as $R\to\infty$. The principal quantum number increases as R decreases. The other asymptotic feature of the curve representing $n(R)$ is the straight line at $R=1.83$. This means that there are no negative energy states in this potential for $R<1.83$.

Since $F(x,\ y,\ 0)=1$ for any x or y, we used the normalization condition

$$\int_0^R \psi^2(r)r^2\,dr=1,$$

and obtained from (3)

$$\psi^2(0,R)=A^2=1\Big/\int_0^R \varphi^2(r)r^2\,dr, \tag{5}$$

where R is the radius of the spherical potential well.

Numerical integration of (5) on a computer yields the values of $\psi^2(0,\ R)$ shown in Fig. 2. As expected, the value of $\psi^2(0,\ R)$ tends asymptotically to the s-electron density $\psi^2(0,\ \infty)$ in the free hydrogen atom as $R\to\infty$. The quantity $\psi^2(0,\ R)$ increases with decreasing R so that, for example, when $R=1.85$, we have $\psi^2(0,\ 1.85)/\psi^2(0;\infty)=2.7$. As expected, the s-electron density increases as the allowed values of R decrease in the case of the electron shell of a neutral atom compressed by the crystal matrix. We may therefore conclude that the electron density around the nucleus of a neutral tin atom in the In_2Te_3 and Ga_2Te_3 matrix should be appreciably greater than $\psi_s^2(0)$ for the free tin atom.

The Mössbauer effect was investigated in[7,8] for the Sn^{119} nuclei isolated in solidified noble gases (Ar, Kr, and Xe) and N_2. It may be supposed that the tin atoms in these matrices are in neutral states with the electron configuration $4d^{10}5s^25p^2$. The isomeric shift turns out to be the same to within experimental error and equal to $+3.21\pm0.01$ mm/sec at 4.2 °K relative to the $BaSnO_3$ source at room temperature. Comparison of this result with the values of δ which we have obtained for In_2Te_3 and Ga_2Te_3 shows that the electron density on the tin nuclei is appreciably higher (~10%) in these cases as compared with the electron density around the tin nuclei in the inert-gas matrices. This difference may be due to the different degree of compression of tin atoms in different matrices. Crystals of solidified gases have a much greater compressibility than In_2Te_3: $\chi_{Kr}=2.9\times10^{-11}$ cm²/dyn, $\chi_{Xe}=2.7\times10^{-11}$ cm²/dyn (4.2 °K), and $\chi_{In_2Te_3}=4.9\times10^{-12}$ cm²/dyn (290 °K). It follows that the tin atoms experience practically no compression in the matrix of solidified gases whereas, in the more rigid In_2Te_3 and Ga_2Te_3 matrix, the compression effect is much greater and leads to an increase in $\psi_s^2(0)$ around the nucleus.

The above experimental data on the values of δ for neutral atoms in two different matrices, and the calculated curve shown in Fig. 2, enable us to estimate the size of the impurity tin atom in In_2Te_3 and Ga_2Te_3. Thus, let us suppose that the change $\Delta\psi_s^2(0)$ associated with the compression effect is due exclusively to the outer 5*s* electrons in the tin atom. The ratio of the isomeric shifts for Ga_2Te_3 (+4.15 mm/sec) and for the tin atom in the argon matrix (+3.65 mm/sec) relative to K_2SnF_6 (reduced to the same temperature)[1] is 1.13, and this corresponds to the density ratio for the outer 5*s* electrons of tin in In_2Te_3, Ga_2Te_3 and the inert gases. We shall suppose that the electron wave function for tin in the solidified gases is the same as for the free undeformed atom. Using the calculated values of $\psi^2(0, R) = f(R)$ (Fig. 2), we can then readily find the effective radius of the tin atom in In_2Te_3 and Ga_2Te_3. It turns out to be 3.9 atomic units. The quantity Z^* is the effective charge for the outer *s* electrons in the tin atom, regarded as a hydrogen-like object. Its value, determined in accordance with the Slater rules,[9] including the screening effect, is 1.7. The radius of the tin atom in In_2Te_3 and Ga_2Te_3 is, therefore, 1.21 ± 0.04 Å, i.e., it is substantially smaller than the crystal-chemical atomic radius of tin reduced to the tetrahedral coordination (1.39 Å).

The size of a compressed impurity atom in an elastic matrix can be determined independently. According to Friedel,[6]

$$\frac{R-r_v}{r_i-R}=\frac{(1+\nu)}{2(1-\nu)}\frac{\chi_m}{\chi_i} \qquad (6)$$

where χ_m and χ_i are the compressibilities of the matrix and the impurity material, and ν is Poisson's ratio for the matrix.

The quantity r_f is the size of the "free" atom, which we shall take to be 1.39 Å (see above), and r_v is the effective size of the tetrahedral void into which the neutral impurity atom is introduced.

The quantity r_v is calculated in[1,2] from thermodynamic data on the solubility of different impurities in In_2Te_3, and turns out to be 0.7 Å. Equation (6) then yields $R = 1.27$ Å (at 290 °K). Naturally, calculations based on (6), which is valid for the elastic continuum model, can hardly pretend to be anything but estimates for R. The agreement between the value of R, calculated from (6) and from the Mössbauer data, can be improved somewhat by taking into account the temperature dependence of χ_m. It is readily shown that, when $r_i > r_v$, $\chi_i(T) = \text{const}$, and $\partial\chi_m/\partial T > 0$, the quantity R is reduced with decreasing temperature. The determination of the value of R from the isomeric shift, given above, is undoubtedly more accurate. The relatively close agreement with the results obtained from the theory of elasticity suggests that this theory can be used in very approximate calculations.

Comparison of the values of δ for neutral atoms in the In_2Te_3, Ga_2Te_3 and inert-gas matrices (in the solid state) enables us to conclude that the difference between the isomeric shifts of the neutral tin atoms is due to differences in the compression of these atoms in different matrices.

The solid state factor introduced in[7] is probably due to this compression. We shall return to this question in a future communication.

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[1] In K_2SnF_6, the tin atom is in the $4d^{10}$ state because the ionicity of the Sn–F bonds is close to unity. The value of δ for K_2SnF_6 relative to the $BaSnO_3$ source is −0.44 mm/sec.[7]

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