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Effective charges of amorphous silicon, germanium, arsenic, and ice

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The mean-square effective charge $e^{*2}=\langle \overleftrightarrow{e}_i : \overleftrightarrow{e}_i \rangle_i$, where $\overleftrightarrow{e}_i$ is the effective charge tensor for the displacement of atom i and $\langle\ \rangle_i$ means the average over all atoms i, has been obtained from the integrated infrared absorptivity of amorphous silicon, germanium, and arsenic. It has also been obtained from the infrared intensity of the translational lattice vibrations of the molecules in ice *I*, which resembles amorphous silicon and germanium in being approximately tetrahedrally coordinated and in being disordered, although with a different kind of disorder. In ice, the root-mean-square effective charge of the molecules is 0.83 electron charges, although they carry only very small equilibrium charges. In contrast, the rms effective charge of the atoms in amorphous silicon agrees, within a considerable uncertainty, with the rms equilibrium charge calculated from molecular orbital theory, but does not exclude a difference of perhaps as much as 30%.

I. INTRODUCTION

Although the atoms at their equilibrium positions in crystalline silicon and germanium and similar substances carry no charge by symmetry, the atoms in their equilibrium positions in amorphous silicon and germanium do carry charges because they lack symmetry. These equilibrium charges have never been measured but have been calculated recently for amorphous silicon using an atomic-orbital model.[1]

When the atoms in amorphous silicon, etc., move from their equilibrium positions, they induce dipole moments. The change $d\vec{\mu}^s$ of the dipole moment of the sample induced by the displacement $d\vec{r}_i$ of atom i is described by the equation

$$d\vec{\mu}_i^s=\overleftrightarrow{e}_i^*\cdot d\vec{r}_i \ , \qquad (1)$$

where $\overleftrightarrow{e}_i^*$ is the effective-charge tensor of atom i. Its elements are defined as

$$e^*_{\alpha\beta,i}=\frac{\partial\mu^s_\alpha}{\partial r_{\beta,i}} \ .$$

The effective-charge tensor so defined describes the dipole moments induced by atomic displacements. It is comprised, therefore, of dipole-moment derivatives and, of course, may not be an actual electrostatic charge, although it has the dimensions of charge. Because a uniform translation of the sample produces no change of dipole moment, the effective-charge tensors are subject to the sum rule

$$\sum_i \overleftrightarrow{e}_i^*=0 \ .$$

The mass-weighted mean-square value $\langle \overleftrightarrow{e}_i^{*2}/m_i\rangle_i$ over all atoms of the effective-charge tensor, where m_i is the mass of atom i and

$$\overleftrightarrow{e}_i^{*2}=\overleftrightarrow{e}_i^*:\overleftrightarrow{e}_i^* \ , \qquad (2)$$

can be obtained experimentally from the intensity of the infrared spectrum. No theoretical value seems to have been calculated. The equilibrium and effective charges are usually represented by tensors of different ranks, the equilibrium charge being a scalar and the effective charge a second-rank tensor. In general, therefore, equilibrium and effective charges are not equal to one another, contrary to a recent suggestion,[1] but they may be if the effective-charge tensor has only equal diagonal elements.

The purpose of this Comment is to determine the root-mean-square effective charges from the infrared spectra of the amorphous elements silicon, germanium, and arsenic, whose crystalline forms have no fundamental infrared absorption, and to compare the value for silicon with the mean value of the actual charge carried by the atoms calculated recently.[1] In addition, the rms effective charge for the translational motions of the water molecules in ice *I*, whose structure is closely related to that of silicon and germanium, has been obtained because it is large, although the equilibrium charges on the molecules are small, and so emphasizes that equilibrium and effective charges may be quite unrelated.

II. THE EFFECTIVE CHARGES

The derivative of the dipole moment $\vec{\mu}$ per unit volume of sample with respect to the normal coordinate Q_k of the kth normal vibration is related to the absorption *by that normal vibration,* for small damping, by the equation

$$\left[\frac{\partial\vec{\mu}}{\partial Q_k}\right]^2=\frac{3c^2}{\pi}\int\left|\frac{3}{\epsilon(\nu)+2}\right|^2 n'(\nu)K_k(\nu)d\nu \tag{3}$$

where $K_k(\nu)$ is the absorptivity at wave number ν due to vibration k defined so that the intensity of light diminishes, due to absorption by vibration k, by the factor $e^{-K_k x}$ after travelling a distance x in the medium, $\epsilon(\nu)$ the complex permittivity at wave number ν, $n'(\nu)$ the real part of the refractive index, and c the speed of light.

Equation (3) can be summed over all vibrations k to give

$$\sum_k\left[\frac{\partial\vec{\mu}}{\partial Q_k}\right]^2=\frac{3c^2}{\pi}\int\left|\frac{3}{[\epsilon(\nu)+2]}\right|^2 n'(\nu)K(\nu)d\nu\ , \tag{4}$$

where K is the absorptivity caused by all the vibrations being considered and the integration is over all these vibrations. For amorphous silicon and germanium, whose refractive index is hardly affected by the vibrational spectrum, the factor $|3/[\epsilon(\nu)+2]|^2 n'(\nu)$ can be put outside the integral sign. For the translational vibrations of ice, however, the lattice vibrations contribute greatly to the refractive index,[2] and then it must be kept within the integral sign.

The atomic displacements can be expanded in the normal coordinates Q_k,

$$\vec{r}_i=m_i^{-1/2}\sum_k \vec{1}_{ik}Q_k\ , \tag{5}$$

where $\vec{1}_{ik}$ is the vector relating the mass-reduced displacement vector $\vec{r}_i$ to the normal coordinate Q_k and is part of the transformation matrix $\vec{1}$, which relates the $3N$ mass-weighted atomic displacements to the $3N$ normal coordinates where N is the number of vibrating particles per unit volume. From Eqs. (1) and (5)

$$\frac{\partial\vec{\mu}_i}{\partial Q_k}=\frac{\overleftrightarrow{e}_i^{*}\cdot\vec{1}_{ik}}{m_i^{1/2}}\ . \tag{6}$$

When this equation is summed over all atoms and squared, and summed over all normal coordinates, remembering that the transformation matrix $\overleftrightarrow{1}$ is orthonormal, the result is

$$\sum_k\left[\frac{\partial\vec{\mu}}{\partial Q_k}\right]^2=N\left\langle\frac{e_i^{*2}}{m_i}\right\rangle_i\ . \tag{7}$$

Equation (7) is identical to Eq. (15) of Ref. (3). From the measured infrared spectrum and Eqs. (4) and (7), the mean-square mass-reduced effective charge of the vibrating particles can be obtained. The only approximations made in the derivation are that the normal vibrations are harmonic and the dipole moment is linear in the displacements. Earlier values[4] of the effective charges were based on an approximate equation.

The integrated absorption intensities of amorphous silicon, germanium, and arsenic and the corresponding root-mean-square effective charges are listed in Table I. The integrated intensity of the translational lattice vibrations of ice, which occur in the range 0–320 cm^{-1}, and the corresponding rms effective charge of the water molecules are also listed for comparison. The equilibrium charges on the atoms or molecules are listed in the fourth column of the table. The equilibrium charge of a water molecule in ice was estimated to first order as follows. Every water molecule is electrically identical with every other, except for orientation, insofar as each has two hydrogen atoms as first atomic neighbors and four oxygen atoms as second neighbors. There are six hydrogen atoms as third neighbors, but they differ from molecule to molecule in their location. Consequently, all molecules are identical up to second atomic neighbors, and so to this approximation have the same charge, which must therefore be zero. The third-neighbor hydrogen atoms cause a variation in charge from molecule to molecule, but its effect is expected to be small.

III. DISCUSSION

The equilibrium and effective charges are, of course, quite different quantities, the equilibrium charge being the total charge on an atom at its equilibrium position and the effective charge the change of the dipole moment of the sample with the displacement of an atom, which is a much

TABLE I. Root-mean-square effective charges of the atoms in amorphous silicon, germanium, arsenic, and of the molecules in ice.

	$\int K d\nu$[a] (10^3 cm^{-2})	$\langle e_i^{*2}\rangle_i^{1/2}$[b] (Electronic charge)	$\langle e_i^2\rangle_i^{1/2}$ (Electronic charge)
Amorphous silicon	110[c]	0.24±∼.0.04	0.19[d]
	77[e]	0.20±∼0.02	
	136[f]	0.26±∼0.06	
Amorphous germanium	27[c]	0.16±∼0.02	
	38[g]	0.20±∼0.02	
	43[h]	0.21±∼0.03	
	41[e]	0.20±∼0.02	
Amorphous arsenic	29[i]	0.25±∼0.02	
Ice	238[j]	0.83±∼0.08	∼0[k]

[a] Obtained by integration of the referenced spectra.

[b] The errors were estimated from the apparent uncertainty of the measured spectra.

[c] Reference 5.

[d] Reference 1.

[e] Reference 6.

[f] Reference 7.

[g] Reference 8.

[h] Reference 9.

[i] Reference 4.

[j] Reference 2. The integral $\int K(\nu)n'(\nu)\,|\,3/[\epsilon(\nu)+2]\,|^2$ over the translational band 0–320 cm^{-1}, is, from the data in Ref. 2, 178 000 cm^{-2}.

[k] See the text.

more complex quantity. To account for the effective charge, both the charge and the dipole moment of each atom and how they change when any atom is displaced must be taken into account. The dipole moment of the sample is

$$\vec{\mu}^s = \sum_p e_p \vec{r}_p \ ,$$

where the sum is over all electrons and nuclei. It is more convenient to convert it to a sum over all atoms by assigning to atom i an equilibrium scalar charge e_i and an equilibrium dipole moment $\vec{\mu}_i$, so that the equilibrium dipole moment of the sample is

$$\vec{\mu}^s = \sum_i e_i \vec{r}_i + \sum_i \vec{\mu}_i \ .$$

The atomic charges and dipole moments are, of course, to some extent arbitrary because the atoms cannot be unambiguously distinguished from one another, and because the dipole moment of a charged atom depends on the origin of the coordinate system. The dipole moment of the sample is, nevertheless, quite unambiguous. When a displacement $dr_{\beta,i}$ of atom i occurs in the β Cartesian direction the dipole moment of the sample in the direction α changes by the amount

$$d\mu_{\alpha,i}^s = e_i \delta_{\alpha\beta} dr_{\beta,i} + \sum_j r_{\alpha,j} \frac{\partial e_j}{\partial r_{\beta,i}} dr_{\beta,i} + \sum_j \frac{\partial \mu_{\alpha,j}}{\partial r_{\beta,i}} dr_{\beta,i} \ , \tag{8}$$

where $(\partial e_j / \partial r_{\beta,i}) dr_{\beta,i}$ and $(\partial \mu_{\alpha,j} / \partial r_{\beta,i}) dr_{\beta,i}$ are the changes of the (real) charge e_j and of the α component of the dipole moment $\vec{\mu}_j$, respectively, of atom j caused by a displacement $dr_{\beta,i}$ of atom i. Only the first term is associated with the displacement of the equilibrium charge of atom i, and the last two terms, which are due to changes in the charge and the dipole moment of atom j caused by the displacement of atom *i*, cause the difference between the equilibrium and effective atomic charges. We can immediately write from Eq. (8) the expression for an element of the effective-charge tensor $\overleftrightarrow{e}^*_i$ defined by Eq. (1) as

$$e^*_{\alpha\beta,i}=e_i\delta_{\alpha\beta}+\sum_j r_{\alpha,j}\frac{\partial e_j}{\partial r_{\beta,i}}+\sum_j\frac{\partial \mu_{\alpha,j}}{\partial r_{\beta,i}}\ , \qquad (9)$$

where $\delta_{\alpha\beta}$ is the Kronecker delta.

The difference between the equilibrium and effective charges of the atoms in ionic crystals is often interpreted approximately by a shell model, in which a dipole moment is generated by the displacement of an outer shell of electrons relative to a core. This model is probably less useful for atomic crystals such as silicon and germanium because the atoms cannot be as clearly distinguished as they can be in, for example, sodium chloride.

An extreme example of the dominance of the last two terms in Eq. (9) is a water molecule in ice, whose rms effective charge for the translational lattice vibrations, according to Table I, is $0.83\pm\sim0.08$ electron charges, while the equilibrium charge is very small. The effective charge is, no doubt, due to the dipole moment of the water molecule and its great enhancement by the electric fields of neighboring molecules and to specific hydrogen-bond interactions. Its value emphasizes the highly polar nature of ice, as is also shown by the TO-LO splitting of the translational vibrations.[10]

Other examples are crystalline selenium and tellurium. Their unit cells contain three atoms, all on crystallographically equivalent sites, and so the atoms carry no permanent charge. They do, however, have an infrared spectrum due to the fundamental atomic vibrations, and so the atoms have finite effective charges.[11]

The several experimental effective charges of silicon and of germanium atoms in their amorphous phases, as listed in the third column of Table I, agree within the apparent uncertainty of 10–20% or so. The effective charge of silicon and the equilibrium charge calculated by approximate molecular orbital methods agree to well within their combined errors, but the uncertainties are high enough to allow a difference of as much as 30% or more of the equilibrium charge. The relation between the equilibrium and effective charges is, therefore, not yet well known.

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