Charge-Density Variation in a Model of Amorphous Silicon

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(Received 22 October 1979)

A population analysis of the one-electron eigenfunctions of random-network models of amorphous silicon shows fluctuations of the net atomic charge of about 0.2 electron units rms. The majority of the charge is calculable from a linear function of the deviations of first-neighbor distance and of the interbond angle from their values in the crystal.

PACS numbers: 71.25.Mg, 61.40.Df, 71.50.+t

In previous publications, we have presented the electronic structure of amorphous silicon as computed for the continuous-random-network model. In this Letter, we show that the electronic structure, insofar as it deviates from that of the crystal, can be partly understood in terms of the distortions of the immediate surroundings of individual atoms.

As described previously,[1] computer programs have been written which generate examples of continuous-random-network models in which every atom is exactly fourfold coordinated, and which satisfy periodic boundary conditions. In all cases dealt with here, the repeating region was initially a cubical portion of a bcc crystal whose edges were three unit cells long, holding 54 atoms, each joined randomly to four of its eight neighbors. By successive modifications of the bond pattern, the energy of the system, as calculated at the minimum of the Keating potential[2] for each pattern, was lowered until further changes seemed to be practically unattainable. At this stage, a particular example was retained as being realistic if its residual angular distortions were sufficiently small, as determined by comparison with experimental measurement[3] of the width of the second-neighbor peak in the radial-distribution function. The model-building program will be published elsewhere. It should suffice now to remark that the success of the program is much enhanced if, during the process of modification, the effects of angle distortions are exaggerated by choosing the ratio of bending to stretching force constants in the Keating potential to be about 2 instead of 0.3 as observed[2] in crystalline Si and Ge.

The orthogonalized linear combination of atomic orbitals method used for the electronic-structure calculation has been fully covered previously.[4,5] We recall only that the periodic models have one-electron eigenfunctions $\psi_m(\vec{k},\vec{r})$ which are linear combinations of Bloch sums $b_{i\alpha}(\vec{k},\vec{r})$, the latter being $3s$- and $3p$-like functions that have been orthogonalized to the $1s$-, . . ., $2p_z$-like Bloch sums formed from core states. This reduction of the basis set (from 9 to 4 per atom) makes it feasible to compute the states of models having 50–100 atoms in the repeating unit with a negligible loss of accuracy.

In *crystalline* silicon, all atoms are equivalent, and it is impossible to assign other than just four valence electrons per atom. In the *amorphous* form, on the contrary, all the atoms are rendered inequivalent by the static fluctuations in environment, and one expects to be able to assign a different charge to each. This has already been shown by Ching and Lin[6] for particular one-electron states in the framework of the present approach. If we write the one-electron eigenfunctions as

$$\psi_m(\vec{k},\vec{r}) = \sum_{\alpha=1}^{N} \sum_{i=1}^{4} V_{i\alpha}{}^{m} b_{i\alpha}(\vec{k},\vec{r})$$

(N being the number of atoms in the repeating unit), then, following Mulliken,[7] a parameter measuring the localization can be defined by

$$P(m,\vec{k}) = [\textstyle\sum_1^N (f_\alpha{}^m - 1/N)^2]^{1/2},$$

where

$$f_\alpha{}^m = \sum_i V_{i\alpha} \sum_{\beta,j} V_{j\beta} O_{\alpha\beta,ij}$$

is the fraction of an electron contributed to atom α from the state m ($O_{\alpha\beta,ij}$ is the overlap integral between orbitals i, centered on atom α, and j, centered on atom β).

We propose the following obvious extension of this analysis. The formal charge state, q_α, of a particular *atom* α can be calculated as

$$q_\alpha = 4 - 2\sum_{m=1}^{2N} f_\alpha{}^m, \tag{1}$$

where the sum is over occupied states, and the factor of 2 comes from the spin-paired double occupancy. The composite result of the analysis is shown in Fig. 1, the data coming from three examples of 54-atom nets. Although the average charge is zero, there are not infrequently atoms which deviate from neutrality by more than 10% of the number of valence electrons, and the standard deviation is about 0.2 electron. Since, as remarked above, this charge is zero in the (ordered) crystal, it has the significance of a "disorder" parameter in the glass. We shall, in what follows, refer to the crystal to define the atomic environment of minimum energy, and shall seek simply to relate the charges to *local* deviations from that environment.

We show first, in Fig. 2, for a typical 54-atom example, how q_α varies with the average distance to the four ligands of α. A correlation is inescapable, and it is also clear that the sign of the charge is the same as that of the deviation of the mean distance from the ideal value, r_0, in the crystal. A similar correlation is shown in Fig. 3, where q_α is plotted against the deviation from the ideal value of the average distance between atom α and its twelve second neighbors. Recall that the variation in second-neighbor distance in the glasses is almost entirely due to variation in interbond *angle*, and observe that, in Fig. 3, the sign of q is the same as the sign of the independent variable. It is then clear that Fig. 3 points to the mean *angle* deviation as the relevant variable, the angles in question being measured between two bonds meeting at the first neighbors of the given atom, not at the atom itself.

We are thus led to try the following function for the charge:

$$q = a\sum_{i=1}^{4}\frac{r_i - r_0}{r_0} + b\sum_{j=1}^{12}(\varphi_j - \varphi_0) + c\ldots, \qquad (2)$$

where $\cos\varphi_0 = -\frac{1}{3}$. The results of a least-squares fit are given in Table I, along with various structural characteristics of the three examples treated.

Examination of Table I shows, first, that the coefficients a and b of the function (2) are fairly closely determined by the fit to 54 points in each case. Second, the variations in a, b, and c from one example to the next are well within their

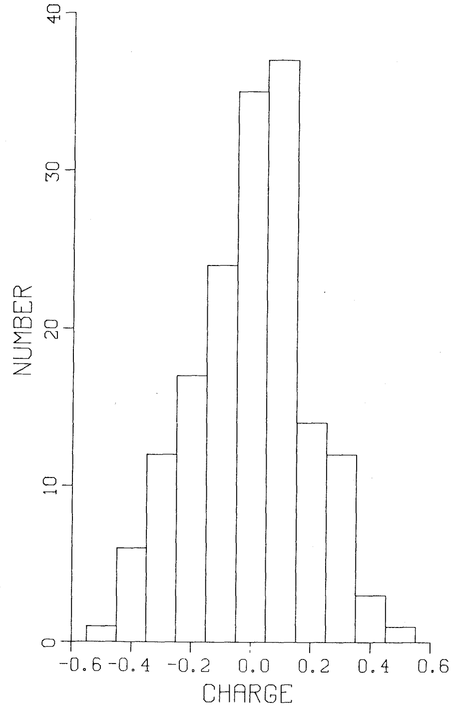

FIG. 1. Histogram of charge distribution for three 54-atom examples. Charge in electron units.

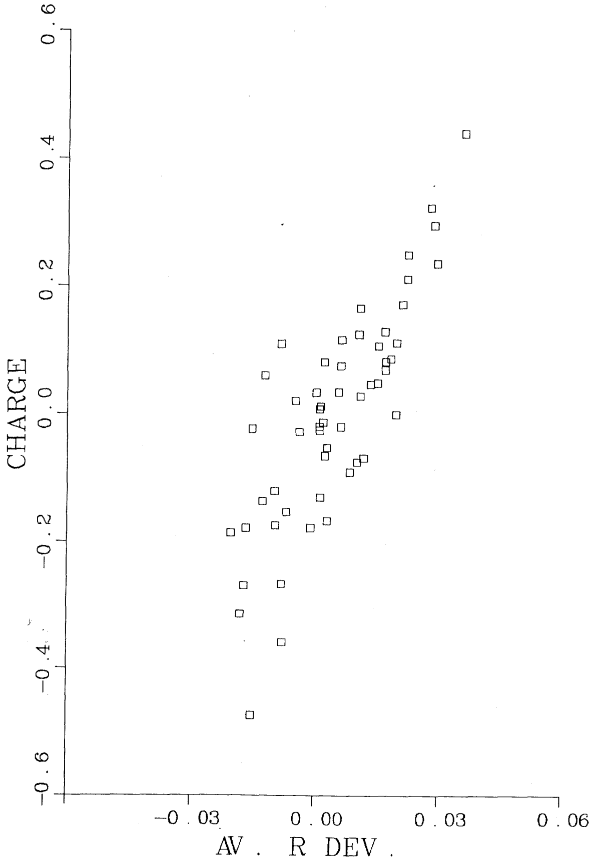

FIG. 2. Variation of charge with average fractional deviation of first-neighbor distance from ideal value.

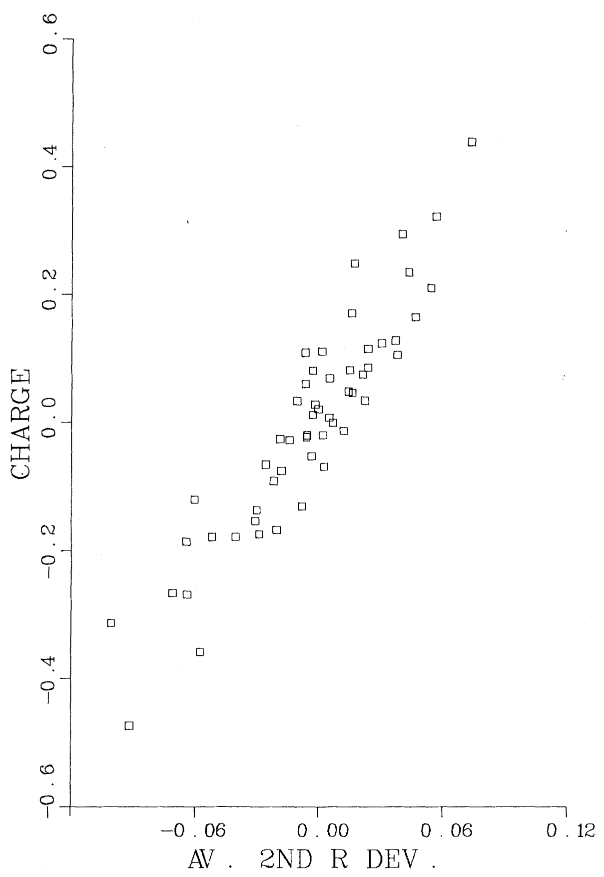

FIG. 3. Variation of charge with average deviation of second neighbor distance from ideal value, in units of ideal bond length.

statistical errors. Third, the constant c is close to zero on the average. Since the examples were constructed quite independently, these facts all speak for a considerable physical basis for (2), which we try to explain below.

The formal charges are affected by the variations in atomic positions in two ways; directly, by the attendant changes in the overlap integrals, and less directly, through the Schrödinger equation, whose solutions produce unequal coefficients on different atoms. The electron excess on atoms whose neighbors are closer to it than the average (Fig. 2) can thus be interpreted either as an increase in overlap of atomic orbitals or as a tendency of the valence electrons to be more dense where the attractive potential is greatest, or as a combination of both. The separation of these effects is beyond the scope of this letter. Some idea of their relative importance can be obtained by summing in (1) over *unoccupied* states. Because of charge conservation, we would have $q \to -q$, and the slopes in Figs. 2 and 3 would be *negative*. Hence, the observed correlations must be largely features of the energetically favored states. The correlation with angle deviation (Fig. 3) suggests strongly a connection with the directionality of the sp^3 hybrids forming the covalent bonds that account naturally for the structure of the amorphous phase.

Since Eq. (2) accounts on the average for over 60% of the computed charges, it seems reasonable to look for other simple geometrical variables that would determine the remainder. For instance, one would expect some influence of the angular distortions at the central atom. We have found no effect linear in the mean angular distortion, and only a small effect quadratic in this variable. Other nonlinear terms have been tried without success. If our continuing efforts along these lines fail, we may be forced to the (unlikely to us) conclusion that the residual charge is determined by functions of the coordinates of four or more atoms. In that event, it will be difficult to get much insight into the physical factors underlying the electronic structure of glasses typified by amorphous Si.

Apart from any attempts at explanation, the charge distribution is accessible experimentally, as shown first by Klug and Whalley.[8] They inferred from the infrared absorption spectera of

TABLE I. Summary of properties of three 54-atom examples of random-network models, and least-squares parameters of Eq. (2).

Model No.	Geometric deviation Bond length (%)	Geometric deviation Angle (rad)	Charge deviation (rms, electron units) From neutrality	Charge deviation (rms, electron units) From calc., Eq. (2)	a	b	c
1	2.3	0.21	0.17	0.07	2.10 ± 0.31	0.174 ± 0.022	-0.018 ± 0.064
2	3.4	0.21	0.21	0.08	1.95 ± 0.23	0.164 ± 0.022	0.027 ± 0.057
3	2.6	0.23	0.19	0.08	2.15 ± 0.37	0.162 ± 0.022	0.028 ± 0.072

amorphous Si and Ge that the atoms carry charges. However, they have interpreted the spectra as giving the average displacements of the atoms from their positions in a crystal, an admittedly unrealistic picture. We suggest the following alternative procedure: The vibrational modes of a specific model can be calculated, as we have done previously.[1] Given the vibrational eigenfunctions and the atomic charges (computed as we have or by an equivalent method) for that model, the dipole matrix elements can be evaluated, and the infrared spectrum can be calculated by averaging over a suitable frequency interval. The result would be subject to the double uncertainties introduced by the incomplete knowledge of the interatomic potential function and by deficiencies in the electronic solution, but the former could be practically eliminated if accurate neutron inelastic-scattering experiments could be performed. The infrared spectrum would thus be a rather direct probe of the electronic structure.

We thank D. D. Koelling, T. S. Gilbert, and A. Rahman for much wise counsel. This work was supported by the U. S. Department of Energy.

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Upper Critical Field of Nb: Calculated Temperature Dependence and Anisotropy

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(Received 11 January 1980)

The magnitude, anisotropy, and temperature dependence of the H_{c2} for Nb are calculated from the underlying electronic structure. Excellent agreement between theory and experiment results if experimental Fermi velocities are used and if Fermi-velocity—anisotropy, strong-coupling, and impurity effects are included.

PACS numbers: 74.70.Lp, 74.70.Dg

The highest magnetic field which a type-II superconductor can sustain in the superconducting state is denoted H_{c2}, the upper critical field. For a given material H_{c2} depends upon sample purity, temperature, and the direction of the applied field relative to the crystal axes. In this paper, the magnitude, anisotropy, and temperature dependence of H_{c2} of Nb are calculated from its electronic structure.

In order to calculate H_{c2} one should include (1) an extension of the usual Ginzburg-Landau-Abrikosov-Gor'kov[1-4] theory to handle the nonlocal effects which enter at temperatures below T_c,[5-12] (2) finite-mean-free-path effects due to impurity scattering,[5-9,11-14] (3) strong-coupling effects,[8,9,14] (4) the wave-vector dependence of the Fermi velocity,[6,10-14] and (5) the anisotropy of the superconducting energy gap.[11-13] The only previous attempt to calculate H_{c2} with use of a realistic model of the band structure was that of Mattheiss,[15] who calculated the enhancement of $H_{c2}(0)$ and of the ratio $\langle H_{c2}(0)\rangle / T_c(dH_{c2}/dT)_{T_c}$ due to Fermi-velocity anisotropy.

Effects (1)–(5) are all included in the following