Solid State Communications, Vol. 45, No. 5, pp. 427–430, 1983.
Printed in Great Britain.

0038–1098/83/050427–04$03.00/0
Pergamon Press Ltd.

CHARGE DISTRIBUTION IN STRUCTURALLY DISORDERED SYSTEMS

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(*Received* 2 *June* 1982 *by M. Cardona*)

In this paper we calculate the charge distribution $n(Q)$ for a structurally disordered system of identical atoms. The atoms have non-zero charges associated to them only because the spatial configuration around each atom is different. The systems considered are those for which an atomic basis set is adequate and an iterative tight binding scheme, where the matrix elements depend on the atomic charges, is used. We study the effect of including explicitly the electrostatic interaction among the charges associated to the atoms in the calculation of $n(Q)$. We propose that the atomic positions of a totally random configuration be modified by amounts proportional to the electrostatic forces on the atoms. We call this a relaxation effect. We find that the new atomic configurations give a narrower $n(Q)$ although they have practically the same energy and radial distribution function as the original configuration.

1. INTRODUCTION

RECENT CALCULATIONS [1, 2] have shown that in disordered systems of identical atoms the atoms acquire different charges due to the differences in the fields around them. Thus a charge distribution $n(Q)$ appears, that gives the number of atoms with charges between Q and $Q + dQ$.

The study of the charge distribution $n(Q)$ can be related to a wide variety of materials, such as for example amorphous Si and Ge, liquid metals and supercritical alkali metals. We will study here a system where the degree of disorder is large, as in the supercritical alkali metals. However the general ideas are also applicable to the other materials.

In a previous paper [2] we calculated $n(Q)$ for a totally random configuration of atoms. For this purpose we used an iterative tight binding method with one orbital per atom in a non-orthogonal basis. In the first iteration we took all diagonal matrix elements equal as the system consisted of identical atoms. The randomness in the atomic positions appeared only in the off diagonal elements through their dependence on the interatomic distances. From the occupied eigenfunctions a formal charge on each atom was calculated which led to modifications in both diagonal and off diagonal matrix elements in the iterative procedure. The iterations were completed when the charge distribution of two successive iterations was identical.

In this paper we will also take into account the direct electrostatic interactions among the charges obtained, which was not considered in our previous work. We will assume that the electrostatic interactions change each atomic position proportionally to the electrostatic force on the corresponding atom. For the new atomic configuration we consider that the whole calculation should be repeated. We call this a relaxation step. If the charge distribution thus obtained differs from that of the previous atomic configuration the relaxation procedure should be continued. We think of this relaxation process as a useful device to obtain a better representation of a disordered system, but it does not imply that the system is first in a totally random configuration and that later in time it relaxes. The interesting result that we obtain in this process is a considerable narrowing of $n(Q)$.

2. METHOD

To simulate the disordered system we average the properties of interest over several random groups of a small number, N, of atoms with periodic boundary conditions. To obtain each distribution a hard core diameter $D = 1.8a^*$ is introduced, a^* being the radius of the outer orbital of the atom. We consider systems where an atomic basis set is adequate and take into account interactions among all pairs of orbitals in a non orthogonal basis [2]. For the case of one atomic orbital per atom, for each random group of N atoms, the system of linear equations to be solved is:

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$$\sum_{j=1}^{N} c_{\mu j}(H_{ij} - E_\mu S_{ij}) = 0 \qquad (1)$$

H_{ij} and S_{ij} are the Hamiltonian and overlap matrix elements, E_μ is the orbital energy and $c_{\mu j}$ the coefficients of the wavefunction. The net charge on each atom is given by:

$$Q_i = 1 - 2\sum_{\mu=1}^{\mu_F} \left[(c'_{\mu i})^2 \Big/ \sum_{j=1}^{N} (c'_{\mu j})^2 \right] \qquad (2)$$

where the first sum is up to the Fermi level and

$$(c'_{\mu i})^2 = \sum_{j=1}^{N} c_{\mu i} c_{\mu j} S_{ij}$$

In order to take into account the intra-atomic electron repulsion, calculations are performed in an iterative way introducing the dependence of both, diagonal and off diagonal, matrix elements on the atomic charges. A simple dependence is the frequency used linear one:

$$H_{ii} = -I - Q_i(I - A) \qquad (3)$$

and

$$H_{ij} = CS_{ij}(H_{ii} + H_{jj})/2 \qquad (4)$$

I being the ionization potential, A the electron affinity and C a parameter with the value $1 < C \leqslant 2$. Iterations are continued until the charges obtained from equation (2) are the same as those used as input in equations (3) and (4).

Other laws are also possible, for example instead of the linear dependence one may propose a stronger dependence of H_{ii} with the charge such as

$$H_{ii} = -I - 2Q_i(I - A)/(1 - Q_i) \qquad (5)$$

This law also gives $-I$ for the diagonal matrix element of the neutral atom and $-A$ for the negatively charged ion. For the positively charged ion law (3) gives probably a too small absolute value while law (5) gives, obviously, an upper limit. However for the system under study the charges Q_i obtained are small and the difference between calculations with equations (3) and (5) is not too large, equation (5) giving a narrower charge distribution $n(Q)$.

For the off diagonal elements instead of equation (4) one may replace the overlap $S_{ij} = S(r)$ by a function $F(r)$ more strongly dependent on the distance [3]. For the 1s orbitals with Bohr radius a^*, used in this work

$$S(r) = e^{-r}(1 + r + r^2/3) \qquad (6)$$

and

$$F(r) = e^{-r}(1 + r) \qquad (7)$$

where r is in units of a^*. The main effect of changing $S(r)$ to $F(r)$ is to change the asymmetry of the charge distribution $n(Q)$. The percentage of atoms with negative charges is less than 50% when using $S(r)$ and becomes larger than 50% with $F(r)$. We do not know at present if $n(Q)$ should be asymmetric and if so, in which sense.

The relaxation proceeds as follows: we move each atom $\Delta\mathbf{r}_i$ provided that if two atoms become closer than D they are left in their original positions. We propose $\Delta\mathbf{r}_i$ to be proportional to the total electrostatic force on atom i:

$$\Delta\mathbf{r}_i = KQ_i \sum_{j \neq i}^{N} Q_j \mathbf{r}_{ij}/r_{ij}^3 \qquad (8)$$

For the new configuation obtained, the previous iterative procedure (equations (1), (2), (3), (4) and (6)) is performed again. With the new set of charges Q_i new $\Delta\mathbf{r}_i$ are calculated with equation (8) and so on. One would be tempted to think that if the relaxation process is carried out a sufficiently large number of steps, or if the parameter K in equation (8) is chosen conveniently, the system will evolve towards an ordered structure (with zero charges for all atoms). This is not so in the procedure used by us for relaxation due to the form of equation (8) and the existence of hard cores, which precisely allow the system to remain amorphous.

3. RESULTS

As in previous work we limit ourselves to two-dimensional systems. We choose several groups of N random points inside a square of length $\rho N^{1/2}$ with periodic boundary conditions. When each new random point is generated, its distance to all previously generated sites is calculated. If any one is smaller than the hard core diameter this new position is rejected. All our calculations use equations (1), (2), (3), (4) and (6). The parameter C in equation (4) is taken $C = 2$ and $A = 0$ in equation (3). Energies are measured in units of I and charges in units of $|e|$. The parameter ρ is the distance between atoms in a square lattice with the same density as the disordered system. For a given type of atoms (that is a given value of a^* with $D = 1.8a^*$) it is obvious that the degree of disorder increases with ρ. We take $\rho = 3a^*$ in our calculations, that is close to the value $\rho \approx 2.5a^*$ for the supercritical alkali metals at the metal–non-metal transition.

In order to decrease the computation time we study first the effect of decreasing the number of random points N in each group with respect to our previous work [2]. We recalculate the charge distribution $n(Q)$ of our previous paper, which used 4 goups with $N = 144$. Using 9 groups with $N = 64$ or 36 groups with $N = 16$ the distributions remain very similar in shape [see Figs. 1(a) and (b)]. Furthermore, the proportion of atoms with charges $|Q| < 0.2$ are, for the groups with $N = 144$,

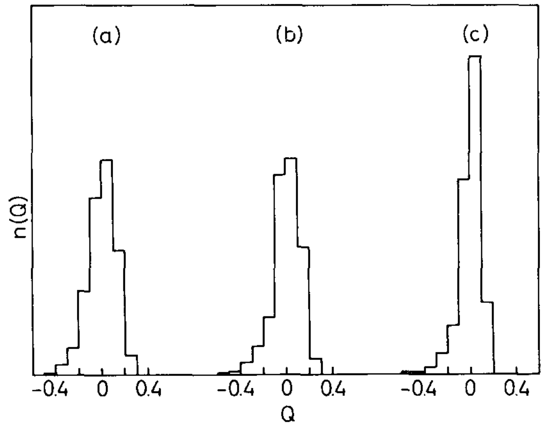

Fig. 1. Charge distribution $n(Q)$ for: (a) Four groups with $N = 144$, unrelaxed. (b) Nine groups with $N = 64$, unrelaxed. (c) Nine groups with $N = 64$, after six relaxation steps.

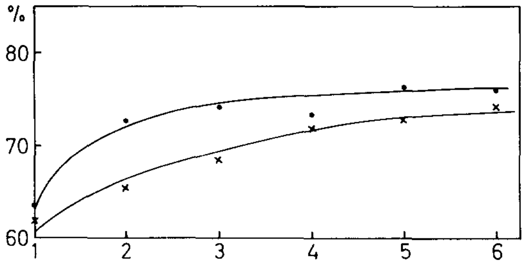

Fig. 2. Percentage of atoms with charges $|Q_i| < 0.1$ as a function of the number of relaxation steps for: ● 9 groups with $N = 64$. x 36 groups with $N = 16$.

$N = 64$ and $N = 16$, respectively 91%, 91% and 92%. Those with $|Q| < 0.1$ are 59%, 64% and 62%, well within the statistical errors. The three effects of the asymmetry: the tail in the negative charge region, the maxima at $Q > 0$ and the proportion of negative charges (46%, 45% and 41% respectively) are present in all calculations. The density of states has approximately the same width in all calculations, the maximum in the same position and the Fermi level practically unchanged. However, in the case with $N = 16$ it presents a dip above the Fermi level that is not present in the larger systems. Therefore, all calculations in this paper are performed for $N = 16$ and $N = 64$.

In Fig. 1(b) and (c) we show the charge distribution $n(Q)$ before relaxation and after six relaxation steps with $K = 1$ in equation (8), for $N = 64$. We see that the relaxation produces a considerable narrowing of the distribution while the asymmetry remains. In Fig. 2 we show this effect in a more quantitative way. We notice that in six relaxation steps the maximum effect has not been achieved but the tendency is clear. The difference between results for $N = 16$ and $N = 64$ may be due, at least in part, to statistical errors.

It is surprising that while $n(Q)$ narrows considerably in the relaxation process the change in the atomic configuration is much more difficult to characterize. Attempts to calculate changes in the radial distribution function and in the entropy failed to give significant differences through relaxation. After six relaxation steps the atomic distribution changes so that the average displacement of an atom from its original position is about 0.1ρ (both for $N = 16$ and $N = 64$) while about 10% of the atoms move more than 0.2ρ. The percentage of pairs of atoms that would come closer than their hard cores and are therefore not moved from their previous step is near 10%. The density of states remains practically unchanged after relaxation with a slight decrease of the high energy tail.

We do not use an energy criterion for relaxation because it is well known that total energy calculations in semi empirical quantum mechanical methods are highly dependent on the approximations and parameters used. Furthermore it is questionable if an electrostatic contribution should be added to the total energy as a separate term. In any case changes in total energy are extremely small through the relaxation process. For example for the calculations for $N = 64$ the sum of eigenenergies over occupied levels is -1.194 per particle and after six relaxation steps it is -1.195. Electrostatic energy goes from 0.012 to 0.005 through relaxation. Thus, at most, the change in total energy would be less than 1%, while the change in $n(Q)$ is obviously much larger.

In conclusion, the relaxation procedure leads to a narrower charge distribution than that of the original totoally random system. However the new atomic configurations are very similar to the original one in radial distribution function, entropy and energy. These results are interesting in relation to model Hamiltonians for amorphous materials where randomness is either postulated in the diagonal and/or off-diagonal matrix elements or some specific geometrical model is assumed for the material and from this the matrix elements are calculated. In particular there has been recently some theoretical [1] and experimental [4] evidence of a charge distribution in amorphous Si. The theoretical work of Gutman *et al.* gives a standard deviation σ for the distribution $n(Q)$ of $0.2e$, while the experiments give 0.07. We shall attempt to explain the origin of this difference from our results for the supercritical alkali metals. First it should be remembered that there is a considerable narrowing of $n(Q)$ within our semi-empirical approach due only to the inclusion of the intra-atomic electron repulsion, in an iterative way. In fact, for the supercritical alkalis we study here σ is 0.18 before iterations (Fig. 3 of [2]) and reduces to 0.13 after the iterative procedure is completed. On the other hand, the calculations for amorphous Si although not semi-empirical but much more elaborate, use a one-electron Hamiltonian and are not self-consistent. Thus it is highly probable that the value of σ obtained in [1] should decrease considerably if some sort of self-consistent or iterative procedure is used. Obviously a further decrease in σ will occur due to the relaxation effect studied in this paper. From Fig. 1(c) we find $\sigma = 0.08$ after relaxation. It is difficult to give an estimate of this effect for amorphous Si as the constraints for relaxation will be different and probably smaller than in the supercritical alkali metals. The very similar values of σ for these two different physical problems is probably a simple coincidence but they suggest that both iterative and relaxation effects should be included in a calculation of the charge distribution $n(Q)$.

Acknowledgements – We thank Dr K.H. Bennemann for a useful conversation on relaxation and Dr M. Cardona for making available to us [4].

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