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Electrostatic Energy of Disordered Distributions of Vacancies or Altervalent Ions

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It is shown that the "average charge" model for calculating the Madelung energy of an ideally disordered crystal gives the correct mean lattice energy, and that only defect terms need be considered in deriving the energy of ordering of a distribution of vacancies or altervalent ions. A completely random arrangement of such defects results in a very large spread of electrostatic potentials at the ion sites, because of the possibility of unreasonable local charge aggregations. Many sites have highly unfavorable potentials, and it is concluded that a completely random disordered arrangement of vacancies or altervalent ions is only possible in very small domains, so that the magnitude of local charge unbalance is limited.

Introduction

Calculation of the electrostatic energy of various crystal lattices has become popular in solid state chemistry and crystallography as an approach to decide between alternative models or to explain order/disorder phenomena.

A recent letter by Giese (*1*) criticizes the method as applied to *disordered* crystals on the grounds

(a) that there are many possible ordered arrangements of ions which give electrostatic energies very close to that of the optimum structure, and very much more favorable than that of the "average charge structure";

(b) that if the average charge model truly represents the fully disordered structure, it is inconceivable from (a) that such a structure exists; and

(c) that the use of an average charge for disordered ions is in any case invalid because on the level of the individual unit cell each ion is unique and cannot conform to some fictitious "average ion."

Giese's letter (*1*) was written in response to our calculations on ixiolite (*2*), where we had already come to his conclusion (b), and had suggested that although apparently disordered, ixiolite in reality consists of small ordered domains which may differ in composition and/or structure. The discrepancy between the energies calculated for ordered and disordered structures has long been known (*3*), but Giese's conclusion (a) now suggests that a mixture of *different* ordered domains will be nearly as stable as a fully ordered equilibrium structure. Examples of such "mixed domains" are multiplying in the solid state literature. Specifically, many

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oxides (*4*) and the iron sulfides (*5*) show domains on a very fine scale. De Bergevin and Brunel (*13*) have drawn attention to the entropy implications of different structures with similar energies.

Mean Lattice Energy

We here address ourselves to the average charge model (conclusion (c)) and show that this model gives the correct mean lattice energies for randomly disordered structures. The individual nature of each unit cell, however, is expressed in the electrostatic potential at an ion site, which may vary greatly from cell to cell.

Bertaut in 1953 (*3*) derived the excess energy of ordering by dividing it up into a periodic and an aperiodic part, the latter depending on the actual distribution of each type of ion. The result was equivalent to the random charge model for a situation involving both vacancies and cation ordering. His method was extended by Brunel and de Bergevin (*12*), but is considerably more complex than the average charge model.

The average ion concept was originally applied to fluorite oxide systems in which up to 12.5% of the oxygen sites are assumed to be vacant in a fully or partially random manner (*6*, *7*). Such an oxide can be easily visualized, and may be used as a model system, assuming the anion lattice to contain a fraction v of vacancies inserted at random. We will not consider the cation lattice, which for simplicity may be assumed to be fully ordered, but with cation charges reduced by the factor $(1 - v)$. In these circumstances the only terms due to the vacancies which affect the mean lattice energy are the potentials at the cation and anion sites due to the anion lattice. (The mean lattice energy involves the sum of all the products of site potentials with the charges occupying those sites). All the anion sites lie on a series of spheres or shells about an anion or cation site. Let the radius of the jth shell be R_j and suppose that it contains N_j sites.

Consider a large number of sites within a fixed anion lattice having a completely random vacancy distribution. The difference ΔV_i between the potential at the ith site calculated on the assumption of the average charge model and the actual value calculated for the assumed vacancy distribution about the site is determined by the differences ΔC_{ij} between the average charge at a site on the jth shell (centered at i) and the average charge calculated over the whole lattice. Now the potential difference between the average and actual distributions, at site i due to the jth shell about i, is $\Delta V_{ij} = (N_j/R_j)\Delta C_{ij}$, and so the overall potential difference at i between the distributions is

$$\Delta V_i = \sum_{j=1}^{k} \frac{N_j}{R_j} \Delta C_{ij}.$$

Thus the mean potential difference over m sites in the same lattice is

$$\overline{\Delta V} = \frac{1}{m} \sum_{i=1}^{m} \sum_{j=1}^{k} \frac{N_j}{R_j} \Delta C_{ij}$$

$$= \sum_{j=1}^{k} \frac{N_j}{R_j} \left(\frac{1}{m} \sum_{i=1}^{m} \Delta C_{ij} \right).$$

But for a large array the mean charge difference $(1/m)\sum_{i=1}^{m} \Delta C_{ij}$ will be zero for each shell j, and hence $\overline{\Delta V} = 0$.

An alternative derivation refers to the potential at a central site averaged over a series of different uncorrelated completely random vacancy distributions, but it gives the same result, that the potential calculated from the average charge model, in which a charge of $-2(1 - v)$ is considered to exist at each anion site, is equivalent to the potential calculated for a random model in which on the average a fraction $1 - v$ of the sites in each shell are occupied by an anion of charge -2.

In the second derivation, assume a random number Y_j of sites on shell j to be occupied (Y_j may be fractional because it is an average over many distributions). The expected value of Y_j is $(1 - v)N_j$. The potential at the center due to ions in shell j is $-2(Y_j/R_j)$. For a random vacancy distribution as above the expected value of V is

$$-2(1-v)\sum_{j=1}^{k}\frac{N_j}{R_j} = (1-v)$$

$$\times \text{ [potential when all sites are occupied].}$$

Both derivations are independent of symmetry or structure, and apply equally to positive or negative ions or to a combination of both, since potentials are additive. There is no restriction on the number of sites N_j in a shell, but the assumption is made that the R_j are the same for fully and partly occupied lattices; i.e., that there is no positional relaxation around a vacancy. This point will be discussed briefly later. It is not the basis of Giese's criticism.

The Relationship between Vacant Site Potentials and Madelung Energies

Madelung energy calculations on vacancy structures are greatly simplified by a relationship which exists between the potentials at vacant sites and the Madelung energy of the lattice. This relationship was used extensively in another paper (*10*) but was not discussed there.

As in the previous section we will take the cation lattice to consist of ions whose charge is reduced by a factor $(1 - v)$ to compensate for the missing anionic charge.

In what follows, superscripts o and d refer to ordered and disordered defect structures, and p to the perfect structure.

The Madelung energy $U^{\rm o}$ of a defect structure with ordered anion vacancies is as follows:

$$U^{\rm o} = -\frac{n}{2}\left[\sum_a^{u-d} Z_a\psi^{\rm o}_{ac} + \sum_c^{u} Z_c(1-v)\psi^{\rm o}_{ca} + \sum_a^{u-d} Z_a\psi^{\rm o*}_{aa} + \sum_c^{u} Z_c(1-v)\psi^{\rm o*}_{cc}\right],$$

where $\psi^{\rm o}_{ac}$ is the potential at an anion site due to the cations in an ordered structure, and the asterisk excludes the self-potential of the ion in the site under consideration. The sums are taken over a unit cell, and the limit $u - d$ refers to unit cell contents excluding vacancies. n is the number of unit cells per mole.

The first two terms refer to cation–anion interactions, and because the energy of an ion in the field of another is the same as the energy of the second in the field of the first, these terms are identical regardless of structure or ionic distribution. The remaining terms refer to anion–anion and cation–cation interactions.

For a disordered structure the Madelung energy is

$$U^{\rm d} = -\frac{n}{2}\left[\sum_a^{u-d} Z_a\psi^{\rm d}_{ac} + \sum_c^{u} Z_c(1-v)\psi^{\rm d}_{ca} + \sum_a^{u-d} Z_a\psi^{\rm d*}_{aa} + \sum_c^{u} Z_c(1-v)\psi^{\rm d*}_{cc}\right].$$

The unit of structure over which the summation is performed must, of course, be large enough to be a fair sample of the disordered structure. Again, the first two terms are identical because of a reciprocity relationship, and since for our model $\psi^{\rm o}_{ac} = \psi^{\rm d}_{ac}$, they are the same as in the ordered case. Similarly $\psi^{\rm o*}_{cc} = \psi^{\rm d*}_{cc}$, so that energies due to cation–cation interactions are the same in $U^{\rm d}$ and $U^{\rm o}$. Only the anion–anion interactions lead to differences between $U^{\rm d}$ and the various $U^{\rm o}$ possible:

$$U^{\rm o} - U^{\rm d} = -\frac{n}{2}\left[\sum_a^{u-d} Z_a(\psi^{\rm o*}_{aa} - \psi^{\rm d*}_{aa})\right].$$

A symbol ψ_{av} is now introduced for the potential which would be added at an anion site if the vacant sites were replenished with anions. Then

$$\psi^{\rm o*}_{aa} = \psi^{\rm p*}_{aa} - \psi^{\rm o}_{av} \quad \text{and} \quad \psi^{\rm d*}_{aa} = \psi^{\rm p*}_{aa} - \psi^{\rm d}_{av}$$

and

$$U^{\rm o} - U^{\rm d} = \frac{n}{2}\left[\sum_a^{u-d} Z_a\psi^{\rm o}_{av} - \sum_a^{u-d} Z_a\psi^{\rm d}_{av}\right].$$

Each sum in this equation concerns the energy gained by the remaining anions due to the change ψ_{av}, in their potential when the vacancies are created. There is again a reciprocity between this energy and an equivalent energy gained by the vacating anions when they are removed from the potential ψ_{va} due to the remaining anions, so that

$$\sum_{a}^{u-d} Z_a \psi^{\mathrm{o}}_{av} = \sum_{a}^{d} Z_a \psi^{\mathrm{o}}_{va},$$

where the superscript, d, indicates that the sum is taken only over the vacant sites in the chosen unit of structure.[1] In the disordered case, the expectation value of ψ^{d}_{va} is no different from $\psi^{\mathrm{d}*}_{aa}$, the potential at remaining anions. Therefore:

$$U^{\mathrm{o}} - U^{\mathrm{d}} = \frac{n}{2}\left[\sum_{a}^{d} Z_a(\psi^{\mathrm{o}}_{va} - \psi^{\mathrm{d}}_{va})\right]$$

$$= \frac{n}{2}\left[\sum_{a}^{d} Z_a(\psi^{\mathrm{o}}_{va} - \psi^{\mathrm{d}*}_{aa})\right].$$

That is, the difference in Madelung energy produced by vacancy ordering is totally reflected in the potentials at the vacant sites due to the remaining anions.

Variance in Potential at Anion Sites, and the Possibility of Random Structures

By considering the variation of potential at sites in the lattice due to a random vacancy arrangement, we can arrive at a new approach to Giese's conclusion (b), that a fully disordered structure cannot exist. This approach arose from a computer simulation model which we set up in an attempt to demonstrate numerically the results of the previous sections. An array of 216 000 sites was represented by 4K 60-bit words. Vacancies were represented by ones and anions by zeroes, and the vacancies were introduced by a masking technique in which vacancies were placed one at a time using a random number generator. Constraints can be easily introduced as required, to ensure that no two vacancies are nearest neighbors or second nearest neighbors.

Unfortunately our array was not big enough to allow convergence of the potential difference ΔV, but the results indicated a surprising variance in the potentials calculated for different sites. The potential at many sites appeared to indicate values which could even have the wrong sign to contain the ions supposedly present there. Introduction of the constraints reducing the degree of disorder reduced the spread of potentials, but even with second nearest neighbor vacancies forbidden, the variation was highly significant.

The variance can be calculated from the second model of the second section using standard sampling arguments for a given total number N of atom sites and a fraction v of vacancies, incorporating the negative correlation between vacancies in any given shell and those in other shells in the lattice. The result (see the Appendix) is

$$\mathrm{Var}(V) = \frac{4v(1-v)}{N-1}\left\{N\sum_{j=1}^{k}\frac{N_j}{R_j^2} - \left(\sum_{j=1}^{k}\frac{N_j}{R_j}\right)^2\right\}.$$

Since for our cubic model the N_j can be obtained from the multiplicities of the indices *hkl* for a cubic lattice, the variance is readily calculable. If the variance is plotted as a function of the radius R of the entire randomly sampled volume (Curve B, Fig. 2), or for large N if it is plotted as a function of the radius R_k of the outer shell being

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[1] This identity is perhaps more obvious if ψ^{o}_{va} and ψ^{o}_{av} are expanded thus:

$$\psi^{\mathrm{o}}_{va'} = \sum_{a \neq a'}^{u-d} \sum_{l}^{\infty} Z_a / |\mathbf{r}_{aa'} + \mathbf{r}_l|$$

and

$$\psi^{\mathrm{o}}_{a'v} = \sum_{a \neq a'}^{d} \sum_{l}^{\infty} Z_a / |\mathbf{r}_{aa'} + \mathbf{r}_l|$$

where $\mathbf{r}_{aa'}$ is the vector separating anion site and vacancy, and $\mathbf{r}_l$ is a lattice vector for the total structure. Each side of the identiy then appears as the same triple sum:

$$\sum_{a'}^{u-d} \sum_{a \neq a}^{d} \sum_{l}^{\infty} Z_a^2 / |\mathbf{r}_{aa'} + \mathbf{r}_l|$$

$$= \sum_{a}^{d} \sum_{a' \neq a}^{u-d} \sum_{l}^{\infty} Z_a^2 / |\mathbf{r}_{aa'} + \mathbf{r}_l|.$$

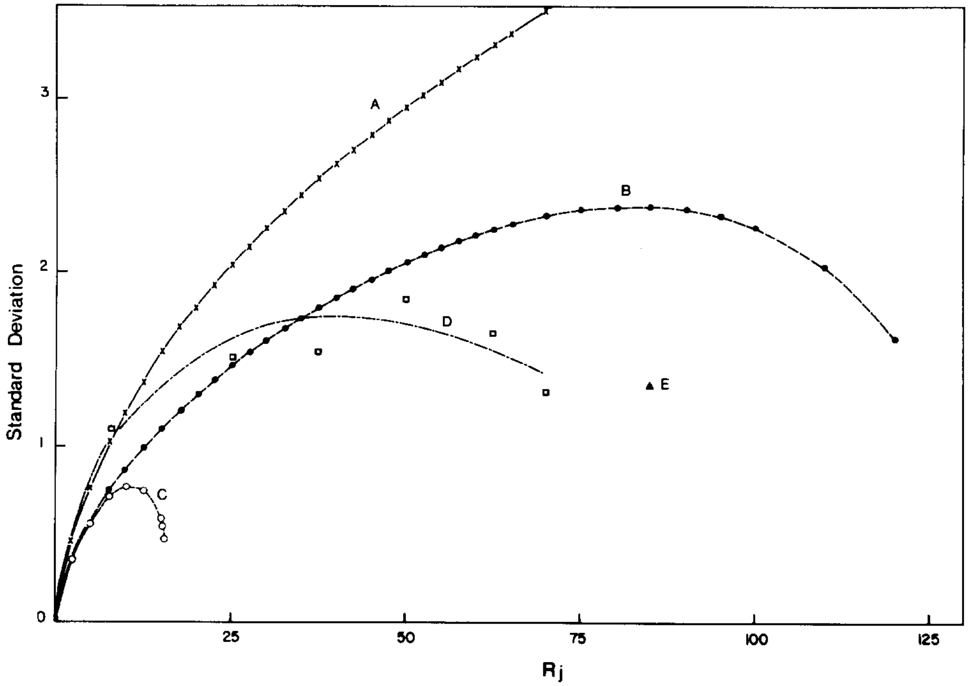

FIG. 1. Cumulative curves showing how the standard deviation of the potential at a site is built up as more and more atoms are considered. R_j is the radius of the last shell included in the calculation. Curve A: random volume infinite. Curve B: radius of random region 120 Å. Curve C: radius of random region 16 Å. The experimental curve for the cubic model has a similar shape (Curve D). A calculated standard deviation for a sphere containing the same total number of atoms as the cube D is shown by point E.

evaluated (related to Curve A, Fig. 1) an approximately linear increase is obtained without limit. Figure 1 shows how the standard deviation is built up shell by shell for large and small N, and Fig. 2 shows the variation of the standard deviation σ with radius of the region. In each case we have 6% vacancies. Similar figures may be derived with somewhat more effort for lower symmetry structures, and the variation of potential at points near the ideal sites can similarly be calculated.

As we pointed out in (*2*), the O^{2-} ion is unstable at potentials below 0.7 units and if we assume an average oxygen site potential of 1.6 units and a Gaussian distribution of deviations we can show that for a σ of only 0.3, the proportion of unsuitable sites becomes significant. When σ reaches 0.5 a significant proportion of the site potentials change sign, so oxygen ions cannot possibly be distributed randomly in this manner. They will be excluded from these unfavorable sites during the formation of the distribution, or at least will lose their charge, thus decreasing still further the effective electrostatic energy of the crystal. Since a σ of 0.3 (0.7) corresponds to a radius of the random region of 7 Å (11 Å), the maximum size for a region of completely random disorder with a proportion of 6% of vacancies is between 7 and 11 Å. For 3% vacancies the radius is between 9 and 17 Å, while for 1% vacancies it is between 40 and 100 Å.

Similar results apply to other anions and to cations, but it should be remembered that this calculated variance is essentially an average (squared deviation from the mean) at a central site over a series of uncorrelated completely random vacancy distributions.

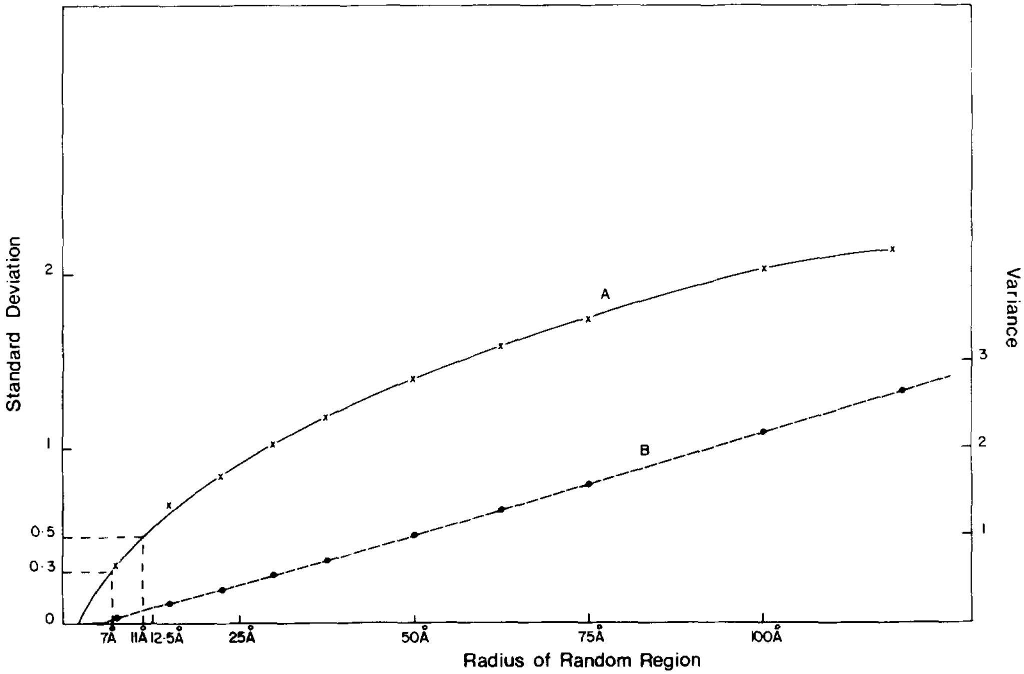

FIG. 2. Variance (Curve B) and standard deviation (Curve A) of the potential at a point in the lattice as a function of the radius of the random region. 6% vacancies.

The variance over a number of sites within a single completely random vacancy distribution will, in general, be lower because potentials at adjacent sites are correlated. The difference between the models should decrease as the size of the distribution increases, and computations using the simulation model (Curve D, Fig. 1) suggest that this difference is not appreciable.

Discussion

What is it that makes a completely random distribution of vacancies or altervalent ions so unfavorable?

One feature of a large region of vacancies arranged completely randomly is that the composition can vary considerably from place to place, and if there is no correlation of anion vacancies with corresponding features of the cation lattice, unacceptable charge separation can occur. If the random regions are limited in size the expected charge separation will decrease, and it may be possible to compensate for these small charge variations by some kind of variable valency mechanism in the cation or anion lattice. Such a structure would represent a fluctuating composition. In Fig. 1, the decrease in standard deviation as the maximum radius is approached is probably the result of a concomitant approach to charge balance.

So far we have assumed all ions to be situated on lattice points; is it possible by relaxing the positions of ions surrounding the charged defect to alter our conclusions concerning site potentials and lattice energy?

Because the relaxation is caused by ions of both signs moving to sites of more favorable potential, the total electrostatic energy of the lattice is increased in magnitude, both because of the improved energy of the moved ions themselves, and because the effect of the vacancy or other defect on the potentials at other sites in the lattice is reduced by the movements. For the latter reason the fluctuation in potential at the ion sites is also reduced by potential relaxation, but a preliminary numerical study of a two-dimensional model indicates that positional relaxation of ions surrounding a vacancy or other defect affects the potential at near neighbors only, since on average there are as many ions moving away from any given site as are moving toward it. Considering the expressions for potential and variance obtained in previous sections, it will be observed that individual terms are relatively more sensitive to a small variation in R_j when R_j is small than when it is large; in addition the shells are much closer together at large R_j so that positive and negative deviations are effectively averaged. Hence where the radius of a random region is large (Fig. 1A), effects of moved near neighbors (i.e., sites near the origin) on the variance of site potentials are negligible, whereas for small domains they may be appreciable (Fig. 1C).

This means that although, as is well known, positional relaxation can appreciably increase the electrostatic energy of a structure containing a completely random arrangement of vacancies or altervalent ions, it cannot significantly improve the variation in site potentials unless the radius of the random region is small. A small random region already has a small spread of potentials (Fig. 2), so it would appear that small random regions may not be too unfavorable from the point of view of either energy or site potentials, especially when relaxation is allowed to occur.

There appears to be only one way to modify our model to allow appreciable volumes containing disordered charged defects, and that is to constrain the degree of randomness of the distribution of defects. It seems likely that interaction of the defects with one another and with the lattice will result in at least a degree of order. The interaction may be due partly to the strain field about a vacancy, which can cause a region of

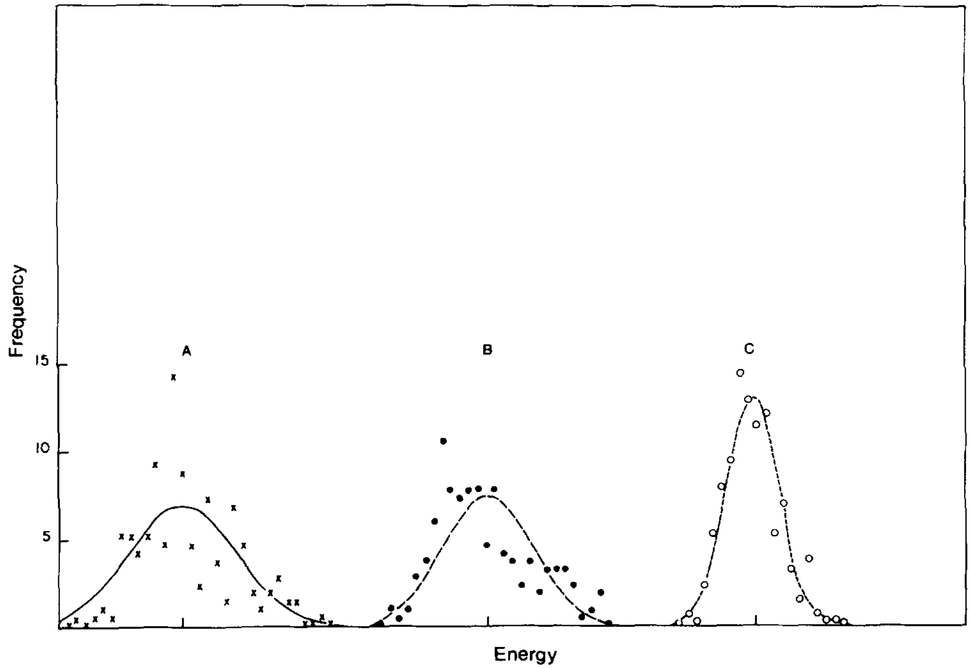

FIG. 3. Distribution of potentials at approximately 200 anion sites in a model lattice compared with normal distribution. Both width at half-height and skewness of the distribution from our limited sample decrease markedly as the vacancies become less random. (A) random, $W_{1/2} = 13.5$, (B) first degree of constraint, $W_{1/2} = 12.2$, (C) second degree of constaint, $W_{1/2} = 7.1$.

exclusion to occur (*8*), and partly to electrostatic interactions, including charge balance requirements over a restricted volume. These effects necessitate a new approach to the thermodynamics of solutions (*9*). The effect of the constraints mentioned in the previous section is shown in Fig. 3, and the exclusion of vacancies from nearest and next nearest sites is seen to reduce the spread of potentials at the anion sites. However, even the second degree of constraint only reduces the width of the distribution by about 50%, so there is considerable stability to be gained by further ordering the vacancies such that their mutual approach is limited, i.e., such that vacancies are dispersed. There are generalized ordering schemes (*10*) applicable to vacancies at any concentration, which effectively set a lower limit on the efficiency with which vacancies are dispersed. Numerous specific examples of such ordered phases may be found in the literature. De Bergevin and Brunel (*13*) have suggested that disorder in ionic structures results from the choice between competing possible structures, a concept that has been extended by Thornber and Graham (*14*) to explain the metamict state.

A study of Ca-stabilized HfO_2 and ZrO_2 has shown (*11*) that these "solid solutions" consist of microdomains as small as 30-Å diameter of ordered calcium compounds within the oxide matrix. There may be different ordering schemes and domain structures in other systems, but we believe that the overall conclusion is inescapable — that even a small amount of ionicity precludes the possibility of a "regular" solid solution of any appreciable extent. For very dilute solutions, an exclusion model may apply (*9*), while an increase of concentration favors domain models of various kinds, culminating in a fully ordered single phase.

Summary

We have shown that the average charge model for calculating the electrostatic energy of a completely randomly disordered crystal formally gives the correct result, although as is well known positional relaxation of surrounding ions will tend to increase the energy toward that of an ordered structure. A simple analysis shows that changes in lattice energy due to changes in vacancy distribution are completely reflected in the vacant site potentials.

In addition, we have shown that many sites in our completely disordered crystal have potentials so unfavorable that the ion which should be present will be unstable there, making the model unrealistic. Positional relaxation does not improve the results unless the completely random region is limited to a volume whose radius is of the order of tens of angstroms. This size limitation seems to be a way of limiting the local charge concentrations inherent in a completely random structure.

An almost inescapable conclusion is that various interactions between charged defects *must* result in a degree of order in any real crystal, and numerical calculations suggest that these interactions probably extend beyond second nearest neighbors in reasonably dilute solutions.

Appendix: Calculation of the Variance

Given a total of N sites in a total of k shells of N_j sites, $j = 1, 2, \ldots, k$, we wish to remove a total of M sites completely at random, where $v = M/N$ is some predetermined fraction (e.g., 0.06).

The number X_j selected from the jth shell to be vacancies has a hypergeometric distribution with

$$\mathrm{prob}(X_j = x) = \frac{\binom{N_j}{x}\binom{N-N_j}{M-x}}{\binom{N}{M}},$$

and so we have

$$E(X_j) = \frac{M}{N} N_j = vN_j,$$

$$\begin{aligned}\mathrm{Var}(X_j) &= M\frac{N_j}{N}\left(1-\frac{N_j}{N}\right)\left(1-\frac{M-1}{N-1}\right)\\ &= \frac{MN_j(N-N_j)(N-M)}{N^2(N-1)}\\ &= \frac{v(1-v)N_j(N-N_j)}{N-1}.\end{aligned}$$

Also the numbers (X_i, X_j) selected from the ith and the jth shells have joint hypergeometric distribution

$$\mathrm{prob}(X_i = u, X_j = x) = \frac{\binom{N_i}{u}\binom{N_j}{x}\binom{N-N_i-N_j}{M-u-x}}{\binom{N}{M}}$$

and we obtain

$$\begin{aligned}\mathrm{Cov}(X_i, X_j) &= \frac{-MN_iN_j(N-M)}{N^2(N-1)}\\ &= \frac{-v(1-v)N_iN_j}{N-1}.\end{aligned}$$

Now the number of ions Y_j remaining in shell j has the same variance as X_j and similarly the covariance between Y_i and Y_j is the same as that between X_i and X_j. Thus we compute the variance of $V = -2\sum_{j=1}^{k}(Y_j/R_j)$ as follows:

$$\begin{aligned}\mathrm{Var}(V) &= 4\sum_{j=1}^{k}\mathrm{Var}\left(\frac{Y_j}{R_j}\right)\\ &\quad + 4\mathop{{\sum}'}_{\substack{i=1\\ i\neq j}}^{k}\sum_{j=1}^{k}\mathrm{Cov}\left(\frac{Y_i}{R_i}, \frac{Y_j}{R_j}\right)\\ &= \frac{4v(1-v)}{N-1}\left\{\sum_{j=1}^{k}\frac{N_j(N-N_j)}{R_j^2}\right.\\ &\quad \left. - \mathop{{\sum}'}_{\substack{i=1\\ i\neq j}}^{k}\sum_{j=1}^{k}\frac{N_iN_j}{R_iR_j}\right\}\\ &= \frac{4v(1-v)}{N-1}\left\{\sum_{j=1}^{k}\frac{NN_j}{R_j^2}\right.\\ &\quad \left. - \sum_{i=1}^{k}\sum_{j=1}^{k}\frac{N_iN_j}{R_iR_j}\right\}\\ &= \frac{4v(1-v)}{N-1}\left\{N\sum_{j=1}^{k}\frac{N_j}{R_j^2}\right.\\ &\quad \left. - \left(\sum_{j=1}^{k}\frac{N_j}{R_j}\right)^2\right\},\end{aligned}$$

as stated in the text.

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