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The Ionic Model Applied to Vacancy Ordering in NaCl-Type Materials

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An order–disorder transition in $Sc_{0.8}S$ (NaCl structure type) was studied by high-temperature X-ray diffraction and 700 ± 20°C was found to be the ordering temperature. A group of ordered sublattices on the rock-salt lattice was generated and a Madelung energy and a configurational entropy were calculated for each assuming the lattice was made up of point charges. Mean field and pair interaction approximations were used to model long-range and short-range orderings, respectively. Results indicate that the ionic model is seriously in error in predicting short-range or long-range orderings of the type observed.

Introduction

A number of early transition-metal chalcides with nominal 1–1 stoichiometry and the rock-salt-type structure have been observed to occur over ranges of homogeneity which can be ascribed to vacancies on the anion or cation sublattice, or both, and have been observed under some conditions to yield ordered sublattices or superstructures. Some examples are TiO (*1*), NbO (*2*), ScS (*3*), ZrS (*4*), and LuS (*5*). The driving force for the ordering processes is not known.

Since the rock-salt-type structure is a prototype ionic structure the occurrence of which has been frequently rationalized by the Born–Haber cycle utilizing ionic charge models to calculate the Madelung energies of the solids, it is of some significance to test the hypothesis that vacancy ordering occurs as the result of coulombic interactions. Such a test is the purpose of the work reported here.

The approach adopted for this test was to calculate the Madelung energies and configurational entropies of a group of ordered sublattices on the rock-salt lattice. In order to keep the group of manageable size it was restricted to cases of single sublattices with cell volumes five times the primitive cell volume of the rock-salt lattice, or less. Of the examples mentioned above only $Sc_{1-x}S$ meets this condition, the remaining cases resulting from yet more complicated vacancy orderings.

The compound $Sc_{1-x}S$ would, however, seem to be a good test for the ionic model, first because of the simplicity of the ordering (described below) and second because of the relatively small participation of *d*-orbitals in the bonding of Sc, the first of the transition metals. The vacancy ordering in $Sc_{1-x}S$ has been described previously (*3*) as resulting in alternating metal layer fractional occupancies in metal atom layers along the body diagonal of the fcc unit cell. Random occupancy within a given plane then results in the space group $R\bar{3}m$.

The vacancy ordering in $Sc_{0.80}S$ was re-

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cently examined by us using high-temperature X-ray diffraction. It was found that weak superstructure lines corresponding to the *R*$\bar{3}$*m* ordering could be observed at temperatures below 700 ± 20°C, but not above, indicating that the order–disorder transition occurs at approximately 700°C. There was no indication of a two-phase region separating the phases, indicating that the transition is second order (*6*). Furthermore the transition from *Fm*3*m* to *R*$\bar{3}$*m* with doubling of the periodicity along the body diagonal of *Fm*3*m* meets all four of the conditions required of a second-order phase change by the Landau theory (*7*).

Results

The sublattices selected for partial occupancy were obtained by the systematic generation of ordered triples of vectors from among the translational symmetry operations of the rock-salt lattice. This procedure yielded sublattices which have reduced occupancy. The resulting sublattices were reduced using the cell reduction procedure (*8*) and the criteria of Niggli (*9*) were utilized to obtain conventional cells and their space group symmetries and all symmetrically equivalent orderings were deleted. The unit cells and space groups are listed in columns 2 and 3 of Table I.

The assumption was made initially that the vacancies within the planes of reduced occupancy are randomly distributed (mean field approximation) and the Madelung energies were calculated by the method of Ewald (*10*) according to

$$U = \sum_{i \neq j} \sum_{j} \frac{q_i q_j}{r_{ij}},$$

where the charges are −2 for the anions and +2.5 (required for neutral $M_{0.8}X$) for the cations, and the configurational entropies were calculated according to

$$S = -R(X_0 \ln X_0 + X_v \ln X_v),$$

where X_0 and X_v are, respectively, the fractions of occupied and vacant metal sites on the partially occupied sublattice. The energy, entropy, and free energy results for the partially ordered solids with 20% of the cation sites vacant are given in columns 4, 5, and 6 of Table I.

The results obtained above include only long-range order. Short-range order entropies were calculated in the pair correlation limit according to (D. K. Hoffman and J. A. Merrick, unpublished results)

$$S_{SR} = \frac{-k}{2} \sum_{i \neq j} \sum_{j} f_{ij}^{(2)}\ f_{ij}^{(2)} \ln [f_{ij}^{(2)}/(f^{(1)})^2],$$

where $f^{(1)}$ is the probability of site occupancy assuming no correlation and where the values of the pair probabilities, $f_{ij}^{(2)}$, were assumed to depend only upon the distance separating the ions. The equilibrium pair correlations were obtained by minimization of the free energy ($A_{SR} = U_{SR} - TS_{SR}$) subject to the constraint that the average fractional occupancy of the cation sites is that of the experimental sample, 0.8. The short-range order energies were observed to overwhelm the short-range configurational entropy to such an extent that the model predicted complete exclusion of occupancy of nearest-neighbor positions, a result inconsistent with the observed symmetry of long-range ordering.

Conclusions

The coulombic model is frequently used in discussions of structure and stability of compounds which crystallize in the NaCl-type structure. This use is generally justified by the observation that the cohesive energies of NaCl-type materials are fairly well calculated by this model. We have shown, however, that the coulombic model fails seriously in the consideration of

TABLE I

THERMODYNAMIC PROPERTIES OF DEFECT–NaCl STRUCTURES

Volume[a]	Space group	Lattice parameters (Å, deg)	$-U$ (kcal mole^{-1})	S (cal mole^{-1} K^{-1})	$\Delta A_{973\text{ K}}$ (kcal mole^{-1})
1	*Fm3m*	$a =$ 5.17	899.0	0.976	0
2	*P4/mmm*	$a =$ 3.65 $c =$ 5.17	915.8	0.663	−16.5
2	$R\bar{3}m$	$a =$ 3.65 $c =$ 17.89	912.1	0.663	−12.8
3	*Immm*	$a =$ 10.96 $b =$ 5.17 $c =$ 3.65	931.2	0.451	−31.8
3	*I4/mmm*	$a =$ 3.65 $c =$ 15.50	917.9	0.451	−18.4
3	*P3m1*	$a =$ 3.65 $c =$ 8.95	904.3	0.451	−4.8
4	*C2/m*	$a =$ 12.11 $b =$ 3.65 $c =$ 6.33 $\beta =$ 100.0	941.2	0.266	−41.5
4	*Pmmm*	$a =$ 5.17 $b =$ 7.30 $c =$ 3.65	937.7	0.266	−38.1
4	*Cmmm*	$a =$ 7.30 $b =$ 10.33 $c =$ 3.65	941.6	0.266	−42.0
4	*P4/mmm*	$a =$ 3.65 $c =$ 10.33	904.3	0.266	−4.6
4	*I4/mmm*	$a =$ 5.17 $c =$ 10.33	949.9	0.266	−50.3
4	$R\bar{3}m$	$a =$ 3.65 $c =$ 35.78	875.9	0.266	3.75
4	*Pm3m*	$a =$ 5.17	949.0	0.266	−49.4
5	*C2/m*	$a =$ 12.11 $b =$ 3.65 $c =$ 8.95 $\beta =$ 119.5	946.2	0.057	−46.4
5	*Immm*	$a =$ 5.17 $b =$ 18.26 $v =$ 3.65	936.3	0.057	−36.5
5	*I4/m*	$a =$ 8.17 $c =$ 5.17	962.6	0.057	−62.8
5	*I4/mmm*	$a =$ 3.65 $b =$ 25.83	875.4	0.057	24.4
5	$R\bar{3}m$	$a =$ 3.65 $c =$ 44.73	827.5	0.057	−72.3

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[a] Volume of generated primitive cell/volume of rock-salt primitive cell.

cation vacancy formation in defect scandium monosulfide in the following ways: (i) the model results in a long-range ordering temperature that is grossly incorrect ($T = \Delta H/\Delta S$ = 42,000 K!); (ii) the model predicts that a variety of long-range ordered solids should be more stable than the observed ordering; and (iii) the model predicts an overwhelming short-range ordering that is not observed. To these facts can be added the observation that the partial molar enthalpy of scandium in the defect solid is overestimated by 115 kcal using ionic model (*11*).

These conclusions are based upon the most simplistic coulombic model, i.e., neglecting repulsive and polarization corrections and a variety of possible short-range effects. However, the comparison of the stabilities of the various possible long-range ordered structures would continue to predict that defect orderings other than the observed $R\bar{3}$ ordering the ScS would be stable even if these correction terms and short-range effects were included and thus it can be safely concluded that the observed long-range ordering does not result from coulombic interactions.

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