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LATTICE STRAINS IN DISORDERED MIXED SALTS

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X-Ray absorption fine structure measurements, and computer simulations were used to solve the structure of mixed salts $\text{RbBr}_x\text{Cl}_{1-x}$. Deviations from the average NaCl structure (nearest neighbor distances and buckling angles) were observed which maximize in the midst of the concentration range. This induces a local elastic strain energy which is the cause of the melting point depression below the linear interpolation. It is shown for the first time that the concentration-weighted average of the Rb-Br and Rb-Cl bond lengths is always greater than the average determined by diffraction. Copyright © 1996 Published by Elsevier Science Ltd.

1. INTRODUCTION

IN ANALYZING the properties of compositionally disordered solids which maintain an average periodic structure the deviations about the average structure are usually neglected. Thus, in a mixed salt like $\text{RbBr}_x\text{Cl}_{1-x}$, it is assumed that the Br and Cl atoms on the anion sublattice are randomly placed at the periodic sites of the NaCl structure with lattice constants determined by diffraction. This approximation has been made out of convenience, since, till recently, deviations of the atoms from their periodic structure has not been known. Recently, a method to accurately determine these deviations for mixed salts has been presented [1]. In this paper it is shown that the deviations are both qualitatively and quantitatively significant. None of the local average distances between atoms coincide with those assumed from the average NaCl structure. Even the compositionally weighted average distance between nearest neighbors is different than the one determined by diffraction. The atomic positions are buckled about the average NaCl structure and this buckling sets up a volume strain energy which has a value that can explain the lowering of the melting temperature below a linear interpolation between the two pure phases. Our results explain why mean field methods have not been

adequate to explain other macroscopic properties and it has been necessary to add empirical corrections to analyze phase diagrams [2] and calculate dielectric [3], spectroscopic [4] and mechanical properties [5].

Our previous x-ray absorption fine structure (XAFS) study [1, 6, 7] has shown that binary mixtures of alkali and silver halides ($\text{RbBr}_{0.62}\text{Cl}_{0.38}$, $\text{Rb}_{0.76}\text{K}_{0.24}\text{Br}$ and $\text{AgBr}_{0.6}\text{Cl}_{0.4}$) are locally distorted (buckled) around the average NaCl structure. (XAFS) method. The compositions were chosen at the congruent melting minimum points of the systems, where liquid and solid are in equilibrium at the same concentration so that solidification from the melt is homogeneous. Here we describe the results of the analysis of $\text{RbBr}_x\text{Cl}_{1-x}$ for different concentrations. Pure RbCl and RbBr were studied in a previous paper [8].

2. EXPERIMENT AND DATA ANALYSIS

Sample preparation is more involved for off-minimum concentrations where inhomogeneities can occur on solidification due to the gap between the liquidus and solidus curves of the phase diagrams [9]. In addition to the sample preparation procedure described in Ref. [6] homogeneity of the samples was assured by alternately grinding, mixing and sintering several times at a temperature 50°C below the melting point until their x-ray diffraction peaks became as sharp as for their pure components. Samples

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were then ground, sieved through a 400 mesh, dusted on Scotch tape and sufficient number of layers were placed together to have an absorption edge step of around one while making the absorption per layer of sample much less than an absorption length. XAFS measurements were performed at the National Synchrotron Light Source (NSLS) using a double crystal Si(111) monochromator. Results for measurements taken for the Rb and Br K edges at 15 K are presented here.

To analyze XAFS spectra we employed the UWXAFS package developed in the University of Washington [10]. First, the smooth embedded atom background $\mu_0(k)$ was removed from the total absorption coefficient $\mu(k)$ (program AUTOBK [11]) and the XAFS signal $\chi(k) = [\mu(k) - \mu_0(k)]/\Delta\mu_0(0)$ was obtained, k being the photoelectron wavenumber, $\Delta\mu_0(0)$ the edge jump. Second, theoretical photoelectron scattering amplitudes and phases were computed for the given systems using the FEFF5 code [12] for the perfect NaCl structure including corrections for use of $\Delta\mu_0(0)$ in the theoretical $\chi(k)$. Theoretical XAFS signals $\chi_{th}(k)$ were calculated for the different photoelectron paths, and it was found that the only significant ones were single-scattering (SS) and collinear focusing double- and triple-scattering (DS and TS) paths. Then nonlinear least square fitting was performed of the theory $\chi_{th}(k)$ to the data $\chi(k)$ with the program FEF-FIT [10]. Several variables were assigned to the theory to account for possible deviations of the local structure from the average [1, 6, 8]. Among them were corrections to the interatomic distances ΔR , mean squared disorder in average distances σ^2 , and rms buckling angles (Θ_{RBR}) and (Θ_{RCR}) between central atom Rb, its 1st nearest neighbor (NN) Br (or Cl), and the 4th NN Rb. It was found that anharmonic corrections were negligible, therefore the pair distribution function is a gaussian. The final values of these variables were obtained from the best fit of theory to data (Fig. 1). Fitting was performed in r space over the range $2.2 \text{ \AA} < r < 7.5 \text{ \AA}$. We were able to analyze the structure through 5 coordination shells.

We took advantage of having measured two edges (Rb and Br) and were able to decrease the number of variables in the fit by constraining the 1st NN bond Rb-Br to have the same length and σ^2 as analyzed from each edge. Composition values of the first coordination shell around Rb and second coordination shell around Br were varied independently. If different, they would have indicated deviations from a random distribution of anions. In our case they agreed within uncertainty of 1.5% with each other and with initial concentration x of the components, indicating that the

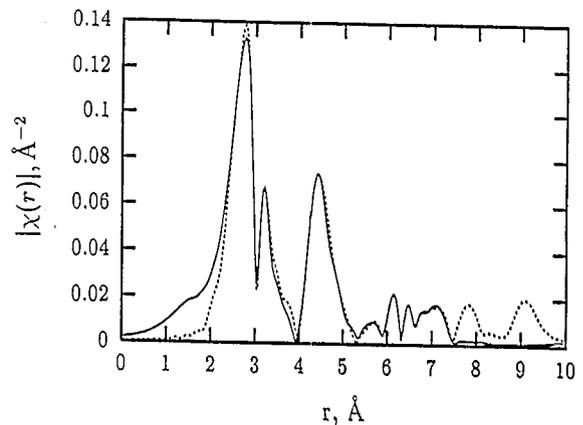


Fig. 1. Fit of the magnitude of the theoretical $\chi_{th}(k)$ (solid) to RbBr_{0.45}Cl_{0.55}Br, Rb edge data (dash).

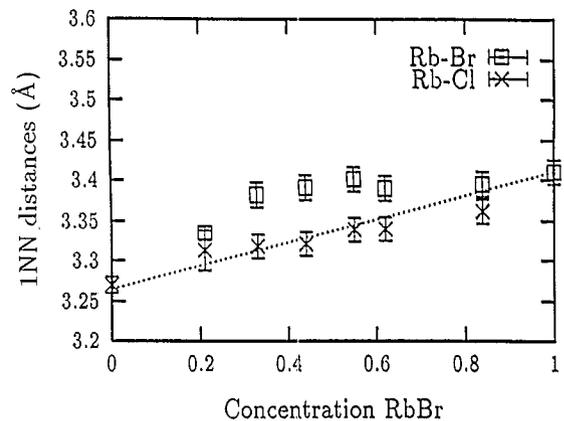


Fig. 2. The average nearest neighbor (NN) distances calculated from diffraction (dash) compared to the local values determined by XAFS for the 1st NN bond lengths.

distribution of Br and Cl in the anion sublattice is completely random for all concentrations. Rb-Br and Rb-Cl 1st NN bond lengths are plotted in Fig. 2. The plot shows dramatically different behavior of the two nearest neighbor distances in the mixture. The longer one, Rb-Br is consistent with results of Sato *et al.* [13] and Frenkel *et al.* [6] and contracts much less when the concentration of Cl increases than the shorter one, Rb-Cl, expands when the concentration of Br increases by the same amount. This asymmetric behavior was noticed before [6] but studied for only one concentration (62% Br). Now we observe the systematic difference in the variation of the two bond lengths with composition. This behavior is as expected since the short range repulsive interaction is much stronger than the long range attractive interaction.

The average 1st NN distance weighted with concentration is significantly greater than the average interplanar distance D obtained from diffraction which

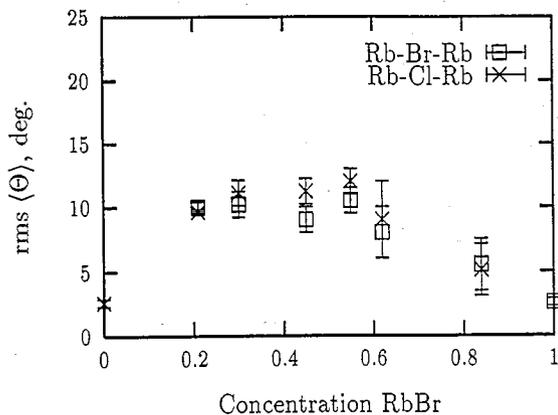


Fig. 3. Buckling angles Rb-Br-Rb and Rb-Cl-Rb versus concentration in $\text{RbBr}_x\text{Cl}_{1-x}$.

is closely given by Vegard's law (i. e., a linear interpolation between the two pure salt values), because the shorter distance expands more than the larger distance contracts. The largest difference is $0.04(1) \text{ \AA}$ for $x \approx 50\%$. Thus, to satisfy both the x-ray diffraction result and the XAFS result for the corresponding bond lengths we must assume that the lattice is buckled about the average structure. Simple geometrical considerations require that

$$D \approx x d_{\text{RB}} \cos\left(\frac{\langle\Theta_{\text{RBR}}\rangle}{2}\right) + (1-x) d_{\text{RC}} \cos\left(\frac{\langle\Theta_{\text{RCR}}\rangle}{2}\right), \quad (1)$$

where d_{RB} and d_{RC} are the average Rb-Br and Rb-Cl bond lengths, respectively. Thus for $x = 0.55$, $\langle\Theta_{\text{RBR}}\rangle$ and $\langle\Theta_{\text{RCR}}\rangle$ should be about $14^\circ \pm 2^\circ$ (assuming, for simplicity, that they are equal to each other) to have our XAFS bond lengths consistent with the x-ray diffraction lattice spacing.

Another independent method to study the bond angles as a function of concentration is through an analysis of the focusing DS and TS paths. These paths are particularly sensitive to slight deviations from collinear arrangement of Rb - 1st NN (Br or Cl) - 4th NN (Rb) and we successfully utilized this property [1, 6, 7] to determine directly the buckling angles. The best fit results for the rms angles $\langle\Theta_{\text{RBR}}\rangle = 10.5^\circ \pm 1.0^\circ$ and $\langle\Theta_{\text{RCR}}\rangle = 12.5^\circ \pm 1.0^\circ$ for 55% Br concentration are in a fairly good agreement with Eq. (1). The rms buckling angles directly determined by the focusing paths as a function of concentration are plotted in Fig. 3. The lattice buckling is dominated by a static distribution of equilibrium positions of atoms since the rms bond angle produced by vibrations at 15 K is 2.6° and thus is a minor perturbation on the static distribution.

3. COMPUTER SIMULATIONS

The XAFS analysis gives only an average of $\langle\Theta^2\rangle$ and to find the actual distribution in Θ we performed a simplified molecular-dynamics (MD) simulation (computer code CLUSTER [6]) of these mixed salts. Potentials were chosen harmonic,

$$V = V_c + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^6 \frac{k_{ij}(r_{ij} - d_{ij})^2}{2}, \quad (2)$$

taking into account only interactions between nearest neighbors separated by r_{ij} , where $d_{ij} = d_{\text{RB}}$ or d_{RC} , is the unstrained position of the bond. Force constants $k_{\text{RB}}, k_{\text{RC}}$ were derived from our XAFS results for σ^2 using the Einstein model [6, 14], V_c is an elastic energy reference level which cancels out when we differentiate Eq. (2) to calculate interatomic forces and velocities. All these quantities are concentration dependent.

The potential determined by XAFS from the partial pair distribution function is the potential of mean force. It is the potential thermally averaged over the positions of all the atoms except the relative positions of the pair of atoms being measured. The k_{ij} is the mean force constant for the i, j pair. This k_{ij} gives a correct value of the average local strain energy of the pair at equilibrium which is the quantity we are interested in determining. The XAFS is not sensitive to V_c . We argue below that V_c varies linearly with concentration as verified by thermodynamic results discussed below, but even if it does not, we are interested in only the local strain energy given by the second term on the right hand side of Eq.(2). The main concentration dependence of V_c comes from the long range elastic strain energy which causes a concentration dependence of the lattice constant in the solid. This long range strain energy is not the strain energy we are interested in since it contributes to V_c . Only the short range forces described by the k_{ij} contribute to the local strain energy of interest. In our computer simulations as discussed below we find that at lowest energy of the solid the r_{ij} are not at the d_{ij} , introducing the strain energy of interest. The lattice constants expansion due to the long range character of the strains is accounted for by fixing the surface of the cubic cluster to have the lattice spacing as given by x-ray diffraction for each composition [15].

Our results were not sensitive to the cluster size, varied from 729 (9^3) up to 4913 (17^3) atoms, indicating that we were obtaining bulk properties. We averaged all characteristics over those inner atoms which are situated at least 2 layers from the surface. Simulation

results for the 1NN bond lengths and rms $\langle \Theta \rangle$ were consistent with the XAFS.

The simulations show that only on the average does the static equilibrium position r_{ij} equal its d_{ij} . The r_{ij} are distributed about the d_{ij} indicating that there is an elastic strain induced in the mixed salt. The XAFS measures the total σ^2 and this static contribution is subtracted from the total σ^2 to find the force constant employed in Eq. (2). The elastic strain is induced by maintenance of both long range order, and the difference between interatomic distances and the corresponding interplanar spacing (lattice parameter), as can be understood by the following considerations.

Let us consider an arbitrary binary alloy $A_xB_{1-x}C$ at low temperature and find the probability for this system to relax to the ground state of the total energy V . The zero point energy is neglected and the minimization of the classical potential of Eq. (2) is considered. For N atoms V depends on $3N - 5$ independent variables. For large N the 5 variables describing rigid displacement and rotation of the alloy are negligible. The minimum of V occurs when $r_{ij} = d_{ij}$ for all pairs, i. e., number of equations is $3N$, equal to the number of variables. Thus, it is possible for a large sample to relax to the ground state ($V \approx V_c$). However, such a buckled system with zero elastic strain energy would not have a long range order which requires additional constraints, namely, that all atom positions deviate only a small fraction of a lattice spacing from the ideal lattice. Therefore, to preserve the long range order in the system, the number of constraints will exceed the number of free variables in the problem, making it impossible to achieve the absolute minimum of the potential energy. The residual potential energy is the energy of strains. Our calculation of the strain energy is shown in Fig. 4. One expects that the functional dependence of $W(x)$ must be of the form $W(x) = W_0x(1-x)$, to the first approximation. A best fit of this form to the points is shown in Fig. 4, where $W_0 = 4.9(4)$ kJ/mole, with the maximum of $1.2(2)$ kJ/mole at $x = 50\%$. Equilibrium atomic positions buckled about the average NaCl structure are shown in Fig. 5.

4. DISCUSSION

Lattice elastic strains play an important role in the thermodynamic properties of mixed salts and cannot be neglected. Because strains exist only in the solid because of the constraint of long range order they will make the liquid more stable relative to the solid and lower the melting point T_m by ΔT_m given by

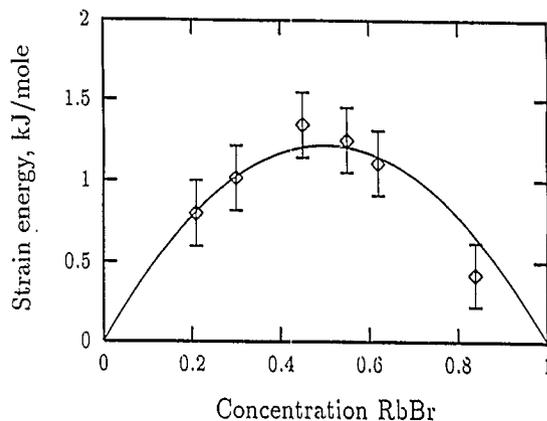


Fig. 4. Strain energy in crystalline $RbBr_xCl_{1-x}$. Shown by the solid curve is the best fit of the parabola $W = W_0x(1-x)$ to the points.

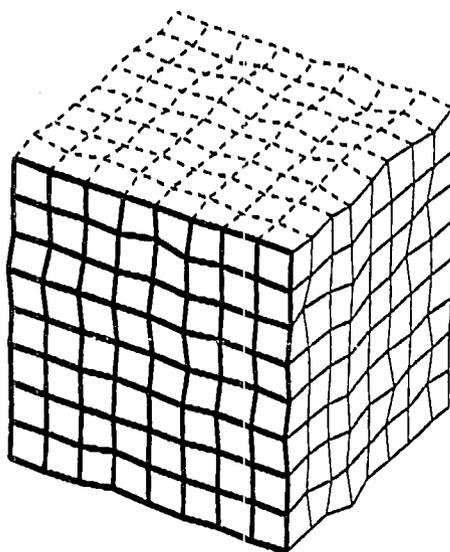


Fig. 5. Equilibrium atomic configurations in $RbBr_{0.55}Cl_{0.45}$.

$$\Delta T_m = \frac{T_m W(T_m)}{q}, \quad (3)$$

where $W(T_m)$ is the elastic strain energy at T_m and q the latent heat of melting of the mixture. Here it is assumed that addition of W to the solid does not affect the other contributions to its free energy, expected since W is less than 0.1 % of the total free energy. The W in Eq. (3) is at T_m , while the value determined experimentally is for 15 K. To estimate the change in W at T_m , it is assumed that this varies with temperature as the bulk modulus, which decreases at T_m to 45 % of its low temperature value [16]. Using this estimate, $W(T_m) = 545$ J/mole. Using the experimental values of $q = 23.5$ kJ/mole and $T_m = 980$ K for the linear interpolation of the pure materials gives $\Delta T_m = 23(3)^\circ\text{C}$. This compares favorably with the experimentally determined value of 25°C .

Without the strain energy the variations of the difference in free energy between the liquid and solid (and thus T_m) is expected to be linear in composition x . The volume of the mixture is linear in x for both liquid and solid and thus the electrostatic and repulsive energies would also be linear for the small volume change, if the contributions of the second term on the right hand side of Eq.(2) were neglected. The strain energy is a consequence of both the local deviations and the average long range order. The entropies of mixing in the liquid and solid are expected to be the same except for volume differences so that their difference should also be a linear function of x . Thus, the conclusion is that the strain energy is the cause of the depression in T_m from the linear interpolation. One consequence of this reasoning is that since the liquid has no strain energy, its internal energy should be linear with x . The deviation from a linear behavior is called the heat of mixing and it is found experimentally for $\text{RbBr}_{0.5}\text{Cl}_{0.5}$ to be $\Delta H_l = 40(5)$ J/mole at T_m ([9, 17]), small compared to $W(T_m)$. The solid, on the other hand has a corresponding value of $\Delta H_s = 530(60)$ J/mole, in good agreement with our estimate for $W(T_m) = 545$ J/mole. It is seen from these results that the heat of mixing of two pure salts is nonlinear with concentration and is mainly caused by local strains, as all other contributions to ΔH should approximately change linearly with x for both solid and liquid phases of the salts.

5. SUMMARY

In conclusion, our precise XAFS measurements have revealed local atomic displacements and bond buckling in $\text{RbBr}_x\text{Cl}_{1-x}$ mixed salts at low temperature. Buckling was strongest in the equimolar region of the concentration. We have shown, for the first time, that the concentration-weighted average of the nearest neighbors bond lengths is substantially greater (0.04(1) Å at the greatest) than the lattice spacing between the two nearest planes. Computer simulations reproduce these results and calculate an elastic strain

energy with a maximum value at $x = 50\%$, the most strongly distorted configuration. Local strains are present only in the solid state and disappear in the liquid state of these mixed salts, and are the major origin of their melting point depression.

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