Buckled Crystalline Structure of Mixed Ionic Salts

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X-ray absorption fine structure (XAFS) measurements of mixed salts $Rb_xK_{1-x}Br$ and $RbBr_yCl_{1-y}$ at their congruent melting points compositions reveal that their actual structure buckles about the NaCl average structure with an rms angular deviation from collinearity of 7°–9°. XAFS measures the buckling directly through three-body correlations, and verifies the homogeneity and randomness of the mixtures. The characteristic ionic sizes are found to be dependent on concentration, causing changes to 0.1 Å in interatom bond distances. A computer simulation based on the information from XAFS and diffraction displays the actual structure of the salts.

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It is generally agreed that a fundamental understanding of the properties of a solid starts with the knowledge of its atomic structure. For pure compounds and elements, generally, especially at low temperature, the position of every atom is on a periodic array. The recently discovered aperiodic crystals are exceptions to this rule but it is believed that the ideal crystals of this type also have perfect long-range order.

When the solid is composed of an alloy or mixture of atoms or molecules over a range of compositions and still remains a single phase, the perfect periodicity is broken by the randomness of the mixing and the difference in the type of atoms. Yet, the average structure still remains periodic and produces sharp Bragg diffraction peaks. However, the actual distribution of atoms usually will not be centered on the periodic lattice. The problem could be further complicated by short range order such as a positive or negative tendency of like atoms to cluster. The issue of the actual location of atoms in such cases relative to the average lattice has not yet, to our knowledge, been addressed experimentally.

In this Letter we investigate this issue for the mixed ionic salts $Rb_xK_{1-x}Br$ and $RbBr_yCl_{1-y}$, where the cations sublattice is disordered in the former and the anion in the latter. The x-ray absorption fine structure (XAFS) technique is used in our investigation because it enables us to obtain both partial pair and three-body correlation functions, which as we show, give sufficient information to completely specify the actual structure.

The two mixtures of interest are soluble in the solid for all compositions. The composition of the mixed salts that were investigated was chosen at the congruent melting point, namely, the minimum of the melting temperature where the liquidus and solidus lines are tangent at their intersection and the solid and liquid have the same equilibrium composition (Fig. 1). This occurs at $x = 0.76$ for $Rb_xK_{1-x}Br$ and $y = 0.62$ for $RbBr_yCl_{1-y}$ [1,2]. For such a composition the solidification occurs at a single temperature, producing a homogeneous single phase solid. The resultant solid was ground and sieved

through 400 mesh. The powder was placed in a quartz tube and heated to 120 °C for several hours while being evacuated by a mechanical pump in order to drive off any absorbed water, and then sealed under vacuum. The container was opened in a dry nitrogen atmosphere, rubbed onto Scotch tape, and then the appropriate number of layers were stacked and sealed in a vacuum tight sample cell under the dry nitrogen atmosphere. The procedure ensured the sample did not contain a significant amount of water.

XAFS measurements were performed at the National Synchrotron Light Source (NSLS) on beamline X11A using a double crystal Si(111) monochromator. Care was taken to eliminate sources of distortion of the XAFS signal (such as minimizing harmonics by detuning the monochromator and making the absorption per layer of sample much less than an absorption length). Measure-
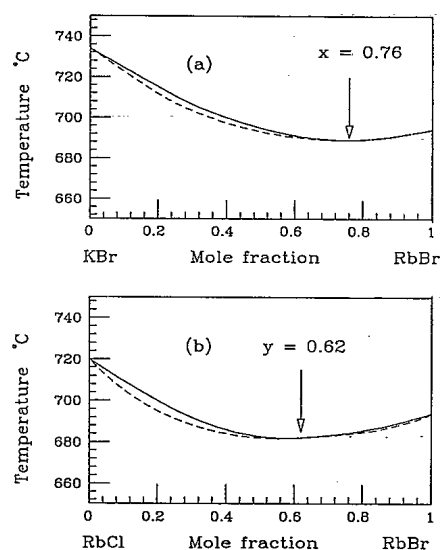

FIG. 1. Phase diagrams of binary mixtures: (a) KBr and RbBr, and (b) RbCl and RbBr. Solid line: liquidus; dashed line: solidus. Arrows indicate the congruent melting minima concentrations.

ments were performed on samples whose temperatures were controlled by a Displex refrigerator. Helium gas within the sample cell (windows of 2 mil Kapton) assured good thermal contact between the Cu cell and the powder samples below liquid nitrogen temperatures.

The XAFS spectra were taken at the Rb and Br K edges of the two mixed salt samples at 30 K. The background was subtracted using the program AUTOBK [3]. A typical resultant normalized XAFS signal $k\chi(k)$ is shown in Fig. 2, where k is the wave number of the photoelectron referenced to the Fermi energy. Both AUTOBK and subsequent fits of the $\chi(k)$ used theoretical calculations of FEFF5 [4]. The theory contains empirical parameters which were determined from the constituent pure salts [5] by enforcing agreement with their known structure.

FEFF5 calculates the contribution to the XAFS of single scattering (SS) and multiple scattering (MS) paths of the photoelectron as it scatters from the surrounding atoms. Since the structure of the mixed salts is, on the average, of NaCl form, and, as we will show, the deviations from this average are small, we could be guided by the analysis of the pure salts to predict which MS paths were negligible, particularly those that have a 90° angle between the outgoing and incoming paths [6]. The end result was that the XAFS signal is dominated by SS paths and those MS paths which are formed by three collinear (or nearly so) atoms. The good agreement that FEFF5 obtains with the pure salts [5], which requires, among others, accurate calculation of the collinear MS paths, gives us confidence that it can also calculate accurately these MS paths when they deviate slightly from collinearity, as in the mixed salts.

The fitting of a theoretical XAFS $\chi(k)$ to the experimental signal was done in r space. The fitting algorithm of the computer code FEFFIT [7] is based on a standard nonlinear least squares technique which minimizes the difference between the Fourier transformed theoretical and experimental χ's. As variables FEFFIT uses the structural characteristics of the sample data: R_i, interatomic distances, σ_i^2, mean square deviations in the half path
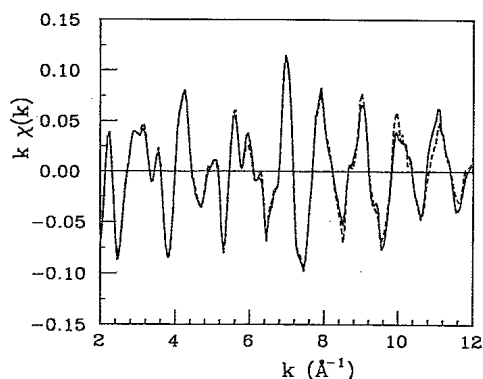

FIG. 2. Normalized absorption $k\chi(k)$ of two independent measurements (dashed and solid) of the Br edge of $Rb_{0.76}K_{0.24}Br$.

lengths (XAFS Debye-Waller factor), and ΔE_i shifts to the E_0 overall, the photoelectron energy origin. An additional parameter S_0^2 (the passive electrons reduction factor for the central atom [8]) was fixed to be the same as that found for the pure salts [5] for each of the two central atoms, namely, 0.91 for Br and 0.98 for Rb.

The accuracy of the analysis was tested by fitting the first neighboring (1nn) shell about the atom of the ordered sublattice, the common Br (Rb) atom. In that case the concentration of the 1nn two anions (cations) must agree with the average composition of the mixture regardless of any tendency to cluster. Indeed an agreement was found for the two salt mixtures within the uncertainty of 1%. Next, the fit was made to the second neighbor (2nn) shell about the Rb (Br) in the disordered sublattice. The composition of the 2nn would differ from x (y) if there were any tendency for clustering. The 2nn is on the same disordered sublattice as the center atom and ascertains the concentration of the two types of atoms that reside on this sublattice. In both mixtures, the compositions determined with 2nn agreed again with x or y within the uncertainty of 1%, indicating that the cations or anions, respectively, are completely randomly distributed in their sublattices, and thus there is no short range ordering.

Up to now the analysis was dominated by only SS. The next interesting shell to be analyzed is the fourth nearest neighbor (4nn) about an atom on the ordered sublattice. In the NaCl structure the 4nn, 1nn, and the center atom are collinear. Such a collinear alignment increases significantly the contribution of the 4nn to the XAFS signal by the forward multiple scatterings through the 1nn intervening atom [9]. This so-called focusing effect turns out to be a very sensitive function of the angular deviation from collinearity and can therefore be used to obtain an accurate measure of it [10,11], as long as it is small enough (less than 20°). By choosing the center atom on the ordered sublattice the 1nn intervening atom is on the disordered sublattice, and thus is of two kind, while the 4nn is the same kind as the center atom. Table I gives the result of such an analysis of the angular deviation from collinearity, $\langle\Theta^2\rangle^{1/2}$. The final fit in r space of $Rb_{0.76}K_{0.24}Br$ (Br edge) to the data is shown in Fig. 3, illustrating the good agreement over the fitting range up to 8 Å.

Also given in Table I are the 4nn, 1nn, and the averaged 1nn distances from the common atom in the two mixtures. The averaging is done over the composition. If the structure had these atoms in a collinear configuration, the 4nn distance would be twice the averaged 1nn distance. Twice the averaged 1nn distance is 0.03 Å larger than the 4nn distance for both samples, consistent with the buckling of the lattice about collinearity. Note that this evidence for buckling is independent of the direct measure of $\langle\Theta^2\rangle$ obtained from the focusing effect.

The other point to note from Table I is the difference of the 1nn distance in the mixed salts from the corre-

TABLE I. Nearest bond lengths r_{1nn} (in Å) and Debye-Waller factors σ^2_{1nn} (in 10^{-3} Å^2) in RbBr, KBr, RbCl (superscript "pure") and their mixtures $Rb_{0.76}K_{0.24}Br$ and $RbBr_{0.62}Cl_{0.38}$ (superscript "mix"). The column $\langle r^{mix}_{1nn} \rangle$ gives the 1nn bond distances averaged over composition. r^{mix}_{4nn} is the fourth neighbor distance (in Å) and the last column gives the buckling angles in degrees.

	Bond	r^{mix}_{1nn}	$\langle r^{mix}_{1nn} \rangle$	r^{pure}_{1nn}	$\sigma^{2(mix)}_{1nn}$	$\sigma^{2(pure)}_{1nn}$	r^{mix}_{4nn}	rms $\langle \Theta \rangle$
$Rb_{0.76}K_{0.24}Br$	Br-Rb	3.39(1)	3.385(10)	3.41(1)	6.0(5)	5.5(5)	6.74(1)	Br-Rb-Br:9.0(1.6)
	Br-K	3.37(1)	3.385(10)	3.27(1)	6.4(5)	6.1(5)	6.74(1)	Br-K-Br:7.7(2.7)
$RbBr_{0.62}Cl_{0.38}$	Rb-Br	3.39(1)	3.371(10)	3.41(1)	6.0(5)	5.5(5)	6.71(1)	Rb-Br-Rb:8.2(1.5)
	Rb-Cl	3.34(1)	3.371(10)	3.27(1)	9.6(5)	5.5(5)	6.71(1)	Rb-Cl-Rb:7.3(3.0)

sponding values of the pure salts and their respective σ^2, mean squared disorder about the distance. For instance, the Br-K 1nn distance changes from 3.27 Å in the pure salt to 3.37 Å in the mixed salt with no significant increase in σ^2. This large change of 0.1 Å with no change in σ^2 indicates that the size of these ions is concentration dependent. Just the fact the bond distance changes is not, by itself, sufficient evidence of a change in size of the ions because, as pointed out by Ashcroft and Mermin [12], the ions may not be "touching." The evidence of touching, though, is reflected by the σ^2 since this is a measure, at the low temperatures of the measurements, of the zero point motion and thus the contact force between atoms. The lack of change in σ^2 indicates the same contact force, and thus "touching" for both distances of this mixture. In contrast, the Rb-Cl 1nn distance increases in the mixed salt over the pure salt by 0.07 Å. Yet the σ^2 also almost doubles (see Table I), suggesting that the contact present in the pure salt is loosened in the mixture and the increase in bond length should not be interpreted as an increase in ionic size. Boyce and Mikkelsen [13] also pointed out that the alkali halide 1nn bonds are functions of concentration but their conclusion that the size of the atoms correspondingly changed was not validated since no check was made on the corresponding changes in σ^2. One expects that the negatively charged Br ion can be distorted more easily than the positively charged K core and thus it is likely that the negative ion has the more variable size.

The XAFS determined the average and mean squared variation, σ^2, of the atomic distances from the center

FIG. 3. Fit of the magnitude of the theoretical $\chi(R)$ (dashed line) to $Rb_{0.76}K_{0.24}Br$, Br edge data (solid line).

atom. It also determined the mean squared angular deviation from collinearity (buckling angle), $\langle \Theta^2 \rangle$, and the random distribution of the atoms on the disordered sublattice. This information, together with the knowledge of the average structure as determined by diffraction, is sufficient to obtain the actual distribution of atoms in the mixture by a molecular dynamics simulation. Since the anharmonicity of the atomic vibrations was found to be negligible at 30 K where the data were taken and analyzed, harmonic potentials between pairs of nearest neighbors were assumed and set to give those values of σ^2 determined for the pure salts [5]. The minima of the potentials were set at the average relative positions determined by XAFS. Our results were not sensitive to assumption of the harmonic potentials, only to the relative positions of the minima.

The structure of the mixed salts was calculated by the molecular-dynamics computer code CLUSTER [14] which gave good agreement with experiment for the simulation of the pure constituent alkali halides [14]. The calculations were performed over both $9 \times 9 \times 9$ (729 atoms), and $11 \times 11 \times 11$ (1331 atoms) clusters in order to check for surface effects. The arbitrary initial configuration of the AB_xC_{1-x} salt was prepared using a random numbers generator for placing the B and C atoms on their average sublattice sites in accordance with the concentration. Atoms A were also placed on their average sublattice. During the simulation, the surface atoms were kept fixed while the internal atoms were allowed to move in accordance with the classical equations of motion and initial random velocities which were rescaled downward several times until the atoms attained a stable equilibrium configuration in the potential minimum. A time step of 10^{-15} s was chosen, which is more than an order of magnitude smaller than the vibrational period. For both clusters averaging was done over the inner $5 \times 5 \times 5$ cluster to exclude the influence of the fixed surface atoms. For the larger cluster, averaging was also done over the inner $7 \times 7 \times 7$ cluster to verify that the averaged region had been immersed into the interior deeply enough to be insulated from surface effects. The final values were obtained by time averaging over 2×10^{-11} s during the last run of the program where the desired equilibrium was achieved. The results obtained in all cases agreed with one another to about 0.1°, indicating that surface effects were negligible.
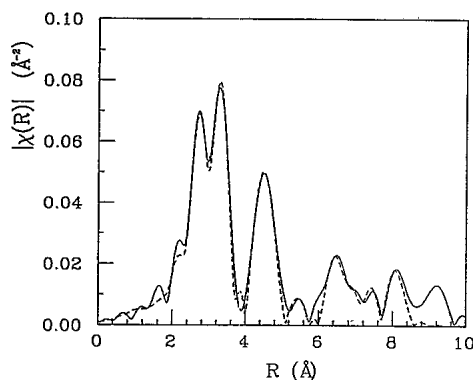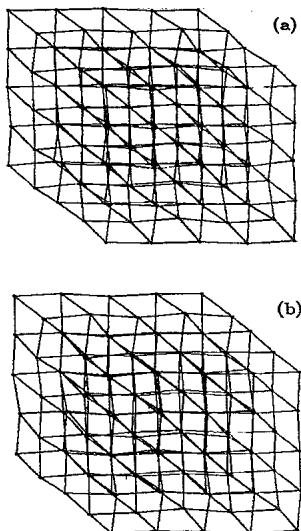
The simulation results were in good agreement

FIG. 4. Equilibrium cluster (inner 125 atoms) configurations of $Rb_{0.76}K_{0.24}Br$ (a) and $RbBr_{0.62}Cl_{0.38}$ (b).

with our XAFS results, e.g., the rms buckling angles were $\Theta(\text{Br-Rb-Br}) = 8.2°$, $\Theta(\text{Br-K-Br}) = 8.0°$ in $Rb_{0.76}K_{0.24}Br$ and $\Theta(\text{Rb-Br-Rb}) = 8.8°$, $\Theta(\text{Rb-Cl-Rb}) = 8.0°$ in $RbBr_{0.62}Cl_{0.38}$, agreeing within uncertainties with the measurements and the uncertainties of the parameters of the model. The resultant structures obtained by the simulation display the actual equilibrium positions of the atoms. Figures 4(a) and 4(b) show the buckled structure within the $Rb_{0.76}K_{0.24}Br$ and $RbBr_{0.62}Cl_{0.38}$ (inner 125 atoms) clusters, respectively.

The fundamental understanding of alloys (and mixed salts) is presently in a rather primitive state. At one empirical level the relative size of the atoms is a parameter that has been correlated with the solubility limits of one with the other. When the size difference exceeds a critical value complete solubility does not occur for all concentrations [15]. At another empirical level, electron per atom ratios are correlated with solubilty limits [16]. On a fundamental level, theoretical approximations have been developed to calculate the electronic properties of alloys, but these models neglect the local deviations from the average structure [17].

It is clear that these distortions are important for understanding the properties of alloys, e.g., the dependence of melting temperature and solubility limits on atomic size differences [18]. Our measurements, however, show that the concept of a rigid atomic size does not apply to the alkali halides, indicating that their understanding requires more sophisticated considerations.

Our XAFS measurements have also shown directly that the actual structure of the mixed salts buckles about the average NaCl structure. This result is possible because XAFS is capable of directly measuring *three* body correlations with high accuracy when the three atoms are near collinearity. The angle of this buckling is a new pa-

rameter which should be added to the characteristics of the structure needed to fully understand the properties of the mixed crystals. It is reasonable to expect that this buckling is a general phenomenon of all disordered lattices.

In conclusion, it is not necessary to be limited in calculating the properties of alloys or mixed salts by simply placing atoms at their average positions. XAFS adds additional information allowing the determination of the actual positions of the atoms in the mixed systems, opening up the prospect of more accurate calculations of the properties of such materials.

[1] J. Sangster and A. D. Pelton, J. Phys. Chem. Ref. Data 16, 509 (1987).

[2] D. Berrebi, L. Grigoryan, S. Rabinovich, E. Shasha, and A. Voronel, J. Phys. Condens. Matter 4, 10139 (1992).

[3] M. Newville, P. Livins, Y. Yacoby, J. J. Rehr, and E. A. Stern, Phys. Rev. B 47, 14126 (1993).

[4] J. J. Rehr, R. C. Albers, and S. I. Zabinsky, Phys. Rev. Lett. 69, 3397 (1992); J. Mustre de Leon, J. J. Rehr, S. I. Zabinsky, and R. C. Albers, Phys. Rev. B 44, 4146 (1991).

[5] A. I. Frenkel, E. A. Stern, M. Qian, and M. Newville, Phys. Rev. B. 48, 12449 (1993).

[6] G. Bunker and E. A. Stern, Phys. Rev. Lett. 52, 1990 (1985).

[7] M. Newville (unpublished).

[8] E. A. Stern and S. M. Heald, in *Handbook on Synchrotron Radiation*, edited by E. E. Koch (North-Holland, New York, 1983), Vol. 1.

[9] P. A. Lee and J. B. Pendry, Phys. Rev. B 11, 2795 (1975).

[10] B.-K. Teo, J. Am. Chem. Soc. 103, 3990 (1981).

[11] B. Rechav, N. Sicron, Y. Yacoby, B. Ravel, M. Newville, and E. A. Stern, Physica (Amsterdam) 209C, 55 (1993).

[12] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders, Philadelphia, 1976), pp. 382–385.

[13] J. Boyce and J. C. Mikkelsen, Jr., Phys. Rev. B 31, 6903 (1985).

[14] A. Frenkel, E. Shasha, O. Gorodetsky, and A. Voronel, Phys. Rev. B 48, 1283 (1993).

[15] A. Voronel, S. Rabinovich, A. Kisliuk, V. Steinberg, and T. Sverbilova, Phys. Rev. Lett. 60, 2402 (1988).

[16] W. Hume-Rothery, J. Inst. Met. 35, 295 (1926); 35, 307 (1926).

[17] See, e.g., *Excitations in Disordered Systems*, edited by F. Thorpe (Plenum, New York, 1981).

[18] S. Rabinovich, A. Voronel, and L. Peretzman, J. Phys. C 21, 5943 (1988).