Local Disorder in Mixed Crystals
as Viewed by XRPD

V. Sh. Machavariani[†1], Yu. Rosenberg[‡], A. Voronel[†], S. Garber[†],
A. Rubstein[†], A. I. Frenkel[*2] and E. A. Stern[§3]

[†]R.&B. Sackler School of Physics and Astronomy, Tel-Aviv University, 69978, Israel
[‡]Wolfson Center for Materials Research, Tel-Aviv University, 69978, Israel
[*]Materials Research Laboratory, University of Illinois at Urbana-Champaign
[§]Physics Department, Box 351560, University of Washington, Seattle, WA 98195-1560, USA

Abstract. A correlation between precise X-ray powder diffraction patterns and atomic size mismatch in disordered mixed crytalls (alloys and ionic crystals) is observed. The anisotropy of the elastic moduli has been taken into account for evaluation of the strain energy density of the mixed crystals revealed in XRPD measurements.

INTRODUCTION

Our extended study of mixed ionic salts with atomic size mismatch RbBr-KBr, RbCl-RbBr, and AgCl-AgBr [1] revealed strong deviations of the local structure obtained by X-ray absorption fine structure (XAFS) technique from the average structure obtained by X-ray powder diffraction (XRPD). The equilibrium atomic positions have been found by the XAFS analysis to be shifted from the periodic lattice sites, ascertained by diffraction. Our further XAFS investigation of the disordered metallic alloy Au_xCu_{1-x} [2] also reveals considerable deviations of the interatomic distances from averaged ones measured by XRPD. In our present careful XRPD investigation we are trying to find the characteristic features of diffraction patterns of crystals with disorder.

Earlier [3] the diffuse scattering of the ordered Cu_3Au alloy were extensively studied. In this paper the alloys with random distribution of the atoms within the crystal lattice are investigated. Typical diffuse intensities [4] are several orders of magnitude below Bragg peak intensities. Therefore, an investigation of the diffuse scattering demands very high signal-to-noise ratio. In the present work we use the width of the Bragg peak itself. This experiment is easier because of large peaks' intensities. Another feature of this work is that we use the XPSD measurement which is easier to do and it can be applied for the wider range of materials than the usual (single crystal) X-ray

521

diffraction. It is especially important for the thin film growth monitoring and for the investigation of the properties of cold-rolled steels. The line widths as a function of diffraction angle have been carefully measured for different concentrations of Au-Cu, Au-Ag, RbBr-RbCl and AgBr-AgCl. A definite correlation has been found between the built in atomic size disorder and the XRPD line broadening in all the investigated mixed crystals.

EXPERIMENTAL

The Au-Cu alloys were quenched to avoid phase separation. The details of samples' preparation were presented in Ref. [1,2]. Homogeneity of the alloys and mixtures was verified by XRPD and no trace of phase separation or superstructure were observed for all the concentrations. The compositions of the mixed samples were established by energy dispersive spectroscopy with a scanning electron microscope. All specimens were found to be homogeneous within the accuracy of 1 %.
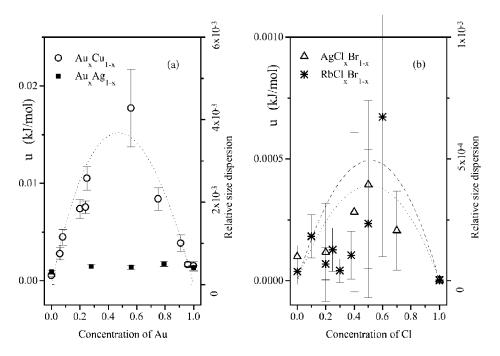

FIGURE 1. Part a: The density of the deformation energy u for Au_xCu_{1-x} and Au_xAg_{1-x} metallic alloys. Dotted (Au-Cu) and dashed (Au-Ag) curves show the relative size dispersion (right scale). Part b: The density of the deformation energy u for $AgCl_xBr_{1-x}$ and $RbCl_xBr_{1-x}$ ionic crystals. Dotted (AgCl-AgBr) and dashed (RbCl-RbBr) curves show the relative size dispersion (right scale).

522

XRPD data were collected in the range 30-120° 2Θ range with CuK_α-radiation on Θ : Θ powder diffractometer "Scintag" equipped with a liquid nitrogen cooled Ge solid state detector. Peak positions and widths of Bragg reflections were determined by self-consistent profile fitting technique with Pearson VII function [5]. Contributions of $K_{\alpha2}$ radiation were subtracted from the total profiles; the obtained results correspond to only the $K_{\alpha1}$component of the K_α-doublet. Lattice constant computation was carried out by a reciprocal lattice parameters refinement.

DISCUSSION

The Williamson-Hall [6] approach allows us to separate two different causes for a line broadening: (i) a finite grain size broadening and (ii) a stress-induced broadening. The usual interpretation scheme [6] assumes that the deformation is uniform in all crystallographic directions. This assumption is doubtful for a crystalline material. It is more physical to consider an anisotropic magnitude of deformation. It was shown earlier [7] that an assumption of uniform deformation pressure gives more adequate picture. However, it may be more reasonable to expect the real parameter of deformation to be a density of a deformation energy u. We compared [8] all the three approaches and found, that the density of the deformation energy better describes the experimental data on mixed alloys.

Fig. 1 presents the calculated density of the deformation energy for the metallic (part a) and non-metallic (part b) samples. One can see from both figures that the maximal deformation energy density roughly corresponds to the 50-50 concentration range. In substitutionaly disordered crystal each site may be occupied either by atom of size d_1 or by that of size d_2 with probabilities $(1-x)$ and x respectively. The relative size dispersion γ can be written as [9]:

$$\gamma = \frac{\left\langle (\Delta d)^2 \right\rangle}{\left\langle d \right\rangle^2} = x(1-x)\frac{(d_1 - d_2)^2}{\left\langle d \right\rangle^2}$$

Indeed, this dispersion has a maximum at 50-50 concentration independent of the disparity of size but its maximal value is greater for the greater disparity. In the case of ionic crystal a distance between anions is a corresponding relevant parameter. Fig. 1 demonstrates the correlation between the density of deformation energy and the size dispersion. In spite of the fact that the relative size dispersion (and, simultaneously, the deformation energy) within the ionic crystals is about an order of magnitude less than in the metallic alloys and is within the uncertainty of our measurements, the results do not contradict a definite correlation between u and the size dispersion.

Another aspect of the results presented here to be noted is that the Au-Cu alloys were rapidly quenched to avoid the thermal equilibrium ordering and phase separation while the Au-Ag alloy and the mixed salts were cooled more slowly, since their disordered phases are thermally stable. Thus, one expects that the quenched alloy would have higher strains than the others, as observed. The microstrains are an inherent feature of the non-thermal equilibrium quenched state and any attempt to

523

anneal them would cause the alloy to change phase. These microstrains are an inherent feature of the disordered alloy at the lower temperatures and their large magnitude is related to the large relative atomic size disparity in the disordered Au-Cu alloys. The energy associated with the microstrains is the important factor in making the disordered phase of Au-Cu alloys thermally unstable at lower temperatures.

CONCLUSIONS

Density of strain energy u for mixed crystals Au-Cu, Au-Ag, AgCl-AgBr and RbCl-RbBr was extracted from our experimental XRPD data. This strain energy density depends on concentration the same way as the relative atomic size dispersion. A definite correlation exists between the line widths of the XRPD pattern and the relative atomic size disparity of the disordered mixed crystals Au-Cu, Au-Ag, AgCl-AgBr and RbCl-RbBr.

REFERENCES

1. Frenkel, A.I., Stern, E.A., Voronel, A., Qian, M., and Newville, M., *Phys. Rev. Lett.* **71**, 3485 (1993); Frenkel, A.I., Stern, E.A., Voronel, A., Qian, M., and Newville, M., *Phys. Rev. B* **49**, 11662 (1994); Frenkel, A.I., Stern, E.A., Voronel, A., and Heald,S., *Solid State Commun.* **99**, 67 (1996); Frenkel, A.I., Voronel, A., Katzir, A., Newville, M., and Stern, E.A., *Physica B* **208-209**, 334 (1995).
2. Frenkel, A.I., Stern, E.A., Rubshtein, A., Voronel, A., and Rosenberg, Yu., *J. Phys. IV* **7**, C2-1005 (1997); Frenkel, A.I., Machavariani, V.Sh., Rubshtein, A., Rosenberg, Yu., Voronel, A., and Stern, E.A., *Phys. Rev. B* **62**, 9364 (2000).
3. Cowley, J.M., *J. Appl. Phys.* **21**, 24 (1950); Warren, B.E., Averbach, B.L., and Roberts, B.W., *J. Appl. Phys.* **22**, 1493 (1951).
4. Welberry, T.R., and Butler, B.D., *Chem. Review* **95**, 2369 (1995).
5. Langford, J., and Louër D., *Rep. Prog. Phys.* **59**, 131 (1996).
6. Williamson, G.K., and Hall, W.H., *Acta Metallurgica.* **1**, 22 (1953).
7. Reimann, K., Würschum R., *J. Appl. Phys.* **81**, 7186 (1997).
8. Rosenberg, Yu., Machavariani, V.Sh., Voronel ,A., Garber, S., Rubstein, A., Frenkel, A.I., and Stern, E.A., *J. Phys.: Condense. Matt.*, **12**, 8081 (2000).
9. Voronel, A., Rabinovich, S., Kisliuk, A., Steinberg, V., and Sverbilova, T., *Phys. Rev. Lett.* **60**, 2402 (1988).