SHORT COMMUNICATIONS

ON THE CALCULATED X-RAY DIFFRACTION POWDER PATTERNS

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STANDARD x-ray diffraction patterns for polycrystalline materials are reported by the National Bureau of Standards, Washington, USA from time to time in two classifications: (i) The experimental x-ray powder diffraction patterns obtained using diffractometers and (ii) the calculated x-ray powder diffraction patterns, computed from published crystal structure data. The motivation for the calculated patterns has been stated to be due to some substances of interest not being readily available for experimental work. In such cases their calculated patterns will be useful. Although the calculated patterns are reported for several crystalline materials, the present note concerns only those patterns of solid solutions or mixed systems in view of their lack of precision due to the negligence of a few factors which are important. One such set of calculated patterns on nine series of solid solutions is reported by Mc Murdie *et al*[1]. The motivation of the present note is to point out certain important factors neglected in the above reported data so that the disagreement between the calculated and actual experimental patterns of the crystalline solid solutions, could be minimized.

In forming a solid solution of element A with element B, two kinds of atoms with different sizes come in contact on a common crystalline lattice. The inclusion of the new substitutional atoms in the crystal causes new centres of disturbances affecting the existing electronic force fields between atoms, both short range and long range, and the resulting effects will be of several kinds[2]. On the atomic scale, both the solvent and solute atoms are shifted from the mean atomic positions in the lattice and thus suffer a permanent static displacement. The static distortion factor arising due to the size effect may be evaluated experimentally from (i) measurement of x-ray diffuse scattering[3] and (ii) measurement of quasi-temperature reduction of Bragg reflections[4,5].

Considering only the Bragg scattering case, relevant for the present consideration of disordered binary substitutional solid solutions, the size differences of the atomic species participating in the crystalline solid solutions cause static displacement for the atoms from their ideal sites. This acts like 'frozen heat motion' when the x-ray diffraction consequence is visualized and introduces a new attenuation factor exp $(-2M')$ for the intensity of the Bragg peaks, over and above the normal Debye-Waller factor[6]. In disordered binary alloy of fcc structures the size effect factor is approximately given by the relationship[6]:

$$2M' = 2B' \sin^2\theta/\lambda^2$$

$$= 48\frac{x}{1-x}(V_A^{1/3} - V_{AB}^{1/3})^2 \sin^2\theta/\lambda^2, \qquad (1)$$

Where x is the atomic fraction of constituent A, V_A is its atomic volume in pure element form and V_{AB} is the average atomic volume in the alloy. Further, for a disordered system obeying Vegard's law for both cell parameters and volumes, it can be shown that the size effect distortion factor may be expressed as:

$$B' = 24(x)(1-x)(a_A - a_B)^2. \qquad (2)$$

The close agreement of this model with the experimental results in Bragg neutron diffraction studies for the crystalline solid solution KBr_xCl_{1-x} has been recently confirmed by Mohanlal et al[7]. The experimental values[7-9] of the size effect distortion factor B' are in the range of 0.34 A^2 to 0.59 A^2 for different compositions of the solid solution KBr_xCl_{1-x}.

The size effect distortion factors, discussed above, have been completely neglected in the calculated x-ray diffraction powder patterns reported by Mc Murdie *et al*[1]. These factors are appreciable when compared with the normal Debye-Waller factors of the crystal. For an intermediate composition of solid solution, the B' values could be about 25% of the normal Debye-Waller factor. It is therefore necessary to consider the distortion factor B' arising due to the size effect of the ions or atoms in any mixed system and may be calculated using a suitable model. The Bragg intensities of various reflections have to be corrected appropriately taking these B' factors as additional attenuating factors apart from the usual corrections for the normal Debye-Waller factors of the crystal, when precision of the calculated patterns is motivated. For solid solutions of cubic systems, even an isotropic

Table 1 *Comparison of typical Debye-Waller factors used in the calculated patterns of solid solutions with reported experimental values*[10-12]

Ion in crystal	Debye-Waller factors (B) in Å^2		
	Calculated patterns for solid solutions	Reported values for pure crystals	Reference
K^+	1.6	K^+ (in KCl) 1.929	10
Na^+ (in KBr-NaBr)	1.6	K^+ (in KBr) 2.550	11
Na^+ (in KCl-NaCl)	1.9	Na^+ (in NaCl) 1.639	12
Br^-	1.6	Br^- (in KBr) 2.200	11
Cl^-	1.6	Cl^- (in KCl) 1.994	10
		Cl^- (in NaCl) 1.326	12

Debye-Waller factor B and size effect factor B' would be adequate for the calculated patterns to obtain more realistic patterns. Further, it must be pointed out that most of the Debye-Waller factors used in the calculations of Mc Murdie *et al*[1] are found to be smaller when compared to the reported values [10-12] even for the end member crystals without size effect considerations. Table 1 indicates typical values of calculated patterns[1] with the values of end member pure crystals reported in the literature[10-12]. In this context, it may be pointed out that the size effect considerations would further increase the deviations appreciably.

Other aspects which have to be considered in the calculated patterns are: (i) deviations from Vegard's law and (ii) miscibility gaps in the solid solution systems. The first factor is important in view of its dependence on the calculated d spacings and since d spacings as well as intensity values are the two main tabulations for the calculated patterns. Deviations from Vegard's law are well known for several systems and have been discussed[13]. The miscibility gaps in several solid solutions are also known; for example, the miscibility gaps in the systems KBr-KI and NaCl-KCl have been reported[14] and therefore, realistic calculated patterns for such systems have to be appropriately prepared. As it is impossible to follow a general approach of considering both these aspects, it may be necessary to look for such data reported in the literature on specific meterial of interest so that a more exact calculated powder pattern for that material could be developed.

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