Acta Cryst. (1956). 9, 466

Local Atomic Displacements in Solid Solutions*

By F. H. Herbstein†, B. S. Borie, Jr.‡ and B. L. Averbach§
Massachusetts Institute of Technology, Cambridge, Massachusetts, U.S.A.

(*Received* 24 *October* 1955 *and in revised form* 5 *January* 1956)

The static displacements of atoms in binary solid solutions from the sites of the average lattice can be determined from measurements of the Bragg intensities. Appreciable local static displacements have been found in the disordered alloys Cu_3Au, CoPt, NiAu and LiMg. For the first three alloys, a good correlation between these measurements and those of the size-effect diffuse scattering was obtained, using a theory which is based on an elastic model of the solid solution. The present measurements also confirm the essential correctness of the atomic displacements previously deduced from diffuse-scattering measurements.

1. Introduction

In disordered solid solutions it seems probable that differences in the radii of the component atoms should result in small random displacements of their centers from the sites of the average lattice. By analogy with the well-known effects produced by thermal displacements, at least two effects would be expected in the X-ray diffraction patterns: (1) the intensities of the Bragg reflections would be reduced by a factor $\exp(-2B' \sin^2 \theta/\lambda^2)$, similar to the Debye temperature factor, and (2) a diffuse scattering would be produced. The magnitude of the quasi-temperature factor and the nature of the diffuse scattering depend on the detailed mechanism by which the lattice is deformed; conversely, experimental measurements of these effects should add to our knowledge of the local atomic structure of disordered solid solutions.

The first theoretical analysis of this problem was made by Huang (1947), who considered dilute solutions only. Huang assumed that the solute atoms behaved as randomly-distributed centers of elastic distortion in the solvent lattice, which was taken to be elastically isotropic. The distance between two atoms in the lattice was then assumed to depend on the distribution of the solute atoms in the vicinity of the lattice vector between the two atoms. However, the identity of the two atoms at the ends of the lattice vector was not taken into consideration. As a consequence of these assumptions, Huang predicted a reduction in the Bragg intensities by a factor $\exp(-2B' \sin^2 \theta/\lambda^2)$, and a diffuse scattering, whose form was given. However, because of the neglect of the nature of the terminal atoms the modulation of the diffuse scattering found by Warren, Averbach & Roberts (1951) was not predicted. A different set of assumptions was used by Warren, Averbach & Roberts, who considered that the interatomic distances in the lattice depend only on the nature of the terminal atoms of the vector and that the effects of the intervening atoms would be lost when averaging over all possible vectors in the solid solution. This analysis was not limited to dilute solutions nor was the existence of short-range order in the solution excluded. The model led to the prediction of a diffuse scattering modulation alone, different in form from that predicted by Huang; the effect of local distortions of this kind on the Bragg intensities was not considered.

Experimental work has now demonstrated the existence of both the quasi-temperature effect on the Bragg reflections and the size-effect diffuse scattering. The former has been reported in the following substitutional solid solutions: Ni–25 atomic % Cu, KCl–KBr (Iveronova, Kuzmina, Futergendler & Deklof, 1951), Cu–32 atomic % Zn (Kurdjumov, Ilina, Kritskaya & Lysak, 1953), Fe–4 atomic % Pd, Fe–5 atomic % Co, Fe–20 atomic % Co (Iveronova & Katcnelson, 1954), Cu–15 atomic % Au (Coyle & Gale, 1955). The size-effect diffuse scattering has been observed in the Au–Ni (Flinn, Averbach & Cohen, 1953), Co–Pt (Rudman, 1955) and Li–Mg (Herbstein & Averbach, 1956) systems and in Cu_3Au (Warren *et al.*, 1951). Although the theoretical analyses described above have been developed for substitutional solid solutions, qualitatively similar effects would be expected in interstitial solid solutions, and experimental evidence of a reduction in the Bragg intensities due to local atomic displacements has recently been reported for dilute interstitial solutions of carbon in α-iron (martensite) (Kurdjumov *et al.*, 1953). There is no experimental evidence at present of the Huang-type diffuse scattering in either substitutional or interstitial solid solutions.

In concentrated solid solutions a complete treatment appears to require both of the assumptions

---

* This work was sponsored by the U.S. Atomic Energy Commission under Contracts AT(30-1)-1002, and AT(30-1)-858.

† Present address: South African Council for Scientific and Industrial Research, Pretoria, South Africa.

‡ Physics Department, Massachusetts Institute of Technology.

§ Metallurgy Department, Massachusetts Institute of Technology.

discussed above, i.e. the distance between two atoms depends on the nature of all the atoms in the vicinity of the lattice vector. The effects on the diffraction pattern of the solid solution would then be expected to be at least threefold: (1) a modulation of the Laue diffuse scattering described by size-effect coefficients, β_i, (2) a quasi-temperature diffuse scattering, (3) a quasi-temperature reduction of the Bragg intensities. These expectations were confirmed in a recent calculation by one of us (Borie, 1955) using an elastic model of the solid solution. In this theory the atomic sites in a crystal of a binary substitutional solid solution of arbitrary composition are considered to be occupied by distortion centers of two kinds, one producing regions of tension and the other of compression. It is assumed that the crystal lattice is perfectly elastic and that the distortion centers are spherically symmetrical. The distortion of the lattice due to the occupancy of a particular site thus follows an inverse square law. That is, if $\mathbf{a}_n$ is the vector position of the nth atomic site in the undistorted crystal, the occupation of the ith site by an A atom causes the nth site to be distorted to the position given by

$$\mathbf{a}_n + c_A \frac{(\mathbf{a}_n - \mathbf{a}_i)}{|\mathbf{a}_n - \mathbf{a}_i|^3}\ ,$$

where c_A is a constant determined by the distortion intensity to be associated with an A atom.

If it is assumed that the distorted position of a site is only slightly different from its undistorted position, so that the net displacement of the site is simply the vector sum of the individual displacements, the actual position of site n in the crystal is given by

$$\mathbf{R}_n = \mathbf{a}_n + \sum_i (c_j) \frac{\mathbf{a}_n - \mathbf{a}_i}{|\mathbf{a}_n - \mathbf{a}_i|^3}\ .$$

The summation is taken over all sites in the crystal except n, and the coefficient, c_j, of each term in the sum is either c_A or c_B depending on whether site i is occupied by an A or a B atom. The distortion constants c_A and c_B are chosen in such a way that the average lattice constant of the crystal is unchanged.

The quantity, $\mathbf{R}_n$, is then inserted into the general intensity expression,

$$I = \sum_m \sum_n f_m f_n \exp\,[ik\,.\,(\mathbf{R}_m - \mathbf{R}_n)]\ ,$$

where I is the scattered X-ray intensity in electron units, f_m and f_n are the atomic structure factors of the occupied sites m and n, $k = 2\pi(\mathbf{S}-\mathbf{S}_0)/\lambda$, and $\mathbf{S}$ and $\mathbf{S}_0$ are the unit vectors defining the incident and diffracted beam directions. If it is assumed that the crystal exhibits no short-range order, the various summations and averages may be evaluated by the methods developed by Huang. The important features of the result are (1) a prediction of sinusoidal modulations of the diffuse scattering analogous to the size effect of Warren *et al.* (1951), (2) a diminution of the integrated intensities of the crystalline reflections by a quasi-temperature exponential factor, (3) an additional quasi-temperature diffuse scattering. This theory does not predict any broadening of the crystalline reflections. The diffuse-scattering modulations and the exponential diminution factor are both related quantitatively to the distortion constants c_A and c_B, and thus to each other. These distortion constants have the dimensions of volume and are related to differences in volume between an A or a B atom and the average atomic volume. A more detailed discussion of the theory will be published at a later date.

In the experimental work cited previously the quasi-temperature effects and the size-effect diffuse-scattering modulations have been shown to exist in different alloys. There was, however, no experimental demonstration of the presence of both effects in the same alloy. In the present work, the quasi-temperature effect was measured in alloys where the size-effect diffuse scattering had already been measured. Since these two effects are related by the theory just presented, a cross-check in terms of two independent measurements was thus possible. The results confirm the essential correctness of the X-ray theory and provide additional evidence that the atoms in a solid solution are displaced from the average lattice sites.

The method employed in this investigation involved the determination of the Debye factor [$\exp(-B\sin^2\theta/\lambda^2)$] at two different temperatures. The difference between these two values of B was then used to compute the Debye temperature Θ_M, from which the thermal displacements of the atoms were obtained. The difference between the measured total displacement and the thermal displacement was presumably due to the local static distortions of the lattice. Values of Θ_M from other sources were used to check the X-ray values of this quantity, but these were not essential to the success of the present method of determining the static displacements since all of the necessary information was obtainable from the X-ray measurements.

The alloys chosen for the measurements were Cu_3Au, CoPt, NiAu (48 atomic % Ni) and LiMg (49 atomic % Li). The first three alloys are face-centered cubic while the last is body-centered cubic. The f.c.c. alloys were all quenched from above their respective critical temperatures to produce the disordered condition; the Li-Mg alloy does not order.

2. Experimental method

(a) *Theory*

Reference should be made to the original papers for a full discussion of the theoretical treatments mentioned in the introduction; we shall consider here only enough theory to make clear the approximations involved in deriving values of B' (distortion) from the measured intensities.

For simplicity the present discussion is limited to disordered f.c.c. crystals but it may easily be extended to other lattice types. The structure factor of a Bragg reflection with indices (*hkl*) is

$$F(hkl) = 4[m_A f_A \exp(-B_A \sin^2\theta/\lambda^2) + m_B f_B \exp(-B_B \sin^2\theta/\lambda^2)]\,, \quad (1)$$

where m_A, m_B are the atomic fractions of A and B in the alloy, f_A and f_B are the atomic scattering factors of A and B atoms at rest, and B_A and B_B are the Debye factors for A and B atoms. Since the unit cell is cubic,

$$B_A = \tfrac{8}{3}\pi^2\overline{u_A^2}\,, \quad (2)$$

where $\overline{u_A^2}$ is the *total* mean-square displacement of A atoms from the sites of the average lattice of the solid solution. The total mean-square displacement is the sum of two terms, one arising from the thermal agitation of the lattice and the other from the local static distortions due to the differences in atomic sizes. The B atoms are treated similarly.

The values of B_A and B_B could in theory be determined from the measured values of $F(hkl)$ and assumed values of the atomic scattering factors by a least-squares analysis of the observational equations (1); at low temperatures, at least, enough (*hkl*) intensities could be measured to make this feasible. However, neither the experimental intensities nor the theoretical atomic scattering factors are known accurately enough for the present application of this method and we have therefore adopted the following simplified procedure. We assume that $B_A = B_B$. Since the X-ray theories do not distinguish between the static displacements of the different kinds of atoms, this implies only that the amplitudes of thermal vibration of both components are the same. There does not appear to be at present any method of estimating the individual vibration amplitudes of atoms in disordered solid solutions. The only experimental data available concern ionic crystals (Lonsdale, 1948), where the individual vibration amplitudes of the components do not differ much even when there is a considerable disparity in their masses. In a disordered solid solution the disparity in the vibration amplitudes of the components would be expected to be less than in an ordered solution so that the approximation appears to be permissible.

If $B_A = B_B$, then (1) can be rewritten as

$$F(hkl) = 4(m_A f_A + m_B f_B) \exp(-B \sin^2\theta/\lambda^2)\,. \quad (3)$$

The value of B can be found by using the theoretical values of the atomic scattering factors and plotting

$$\ln\left[\frac{F_c}{F_o}\right] \equiv \ln\left[\frac{4(m_A f_A + m_B f_B)}{F(hkl)}\right] \text{ versus } \frac{\sin^2\theta}{\lambda^2}\,.$$

The slope of the resultant straight line gives B directly. In the present set of experiments, the Debye factor was measured at room temperature and at liquid-nitrogen temperature. From the difference between these two values of B, the Debye temperature can be obtained as follows (James, 1948, p. 219):

$$\Theta_M = \left\{\frac{6h^2[T_1\{\varphi(\chi_1)+\frac{1}{4}\chi_1\} - T_2\{\varphi(\chi_2)+\frac{1}{4}\chi_2\}]}{mk(B_1-B_2)}\right\}^{\frac{1}{2}}, \quad (4)$$

where T_1, T_2 are 300° K. and 90° K. respectively, B_1, B_2 are the experimental Debye factors at these two temperatures, h is Planck's constant, k is Boltzman's constant, $\chi = \Theta_M/T$, and $\varphi(\chi)$ is the Debye integral. The Debye–Waller theory applies strictly only to isotropic, monatomic cubic crystals, and the value of m in equation (4) was taken as the weighted average mass. It is also assumed that neither Θ_M nor B' (distortion) vary significantly in the temperature range considered. B (thermal) was then computed from Θ_M (James, 1948) and B' (distortion) from the difference between B (measured) and B (thermal).

(*b*) *Sample preparation*

The X-ray measurements were made on compressed powder-briquette samples. The surfaces were polished to prevent surface-roughness effects, and all samples were checked by back-reflection photographs for small grain-size and freedom from cold work, and by relative intensity measurements for the absence of preferred orientation. The Cu_3Au sample was quenched into water from 500° C., the CoPt sample from 860° C., the NiAu sample from 900° C., and the LiMg sample from 200° C. No superlattice or precipitate diffraction lines could be detected after these treatments, and the short-range order after these treatments has been reported in the references on diffuse scattering cited previously.

(*c*) *X-ray measurements*

Intensities were measured on an automatic Geiger counter spectrometer, using chart recording. Particular care was taken in the establishment of the background by continuing measurements for some distance on either side of the reflections. The input voltage to the X-ray set was stabilized. Mo $K\alpha$ radiation was used in order to permit measurements at the highest possible values of $\sin\theta/\lambda$. Filtering was achieved by placing a Zr filter on the receiving slit of the Geiger tube in order to remove both the $K\beta$ and fluorescent radiation from the sample. Mo radiation was not suitable for use with the LiMg sample because of the very low absorption coefficient of this alloy, and Cu $K\alpha$ filtered with Ni was used instead. The usual symmetrical reflection geometry was used in order to maintain a constant absorption factor.

The probable error of an individual structure-factor measurement was about ±1% when considered in terms of reproducibility, but the measured structure factors deviated considerably more from a smooth curve; in this sense the probable error of the structure-factor values is about ±4%. These errors were systematic and arose from the fact that the samples were not perfect powder samples. Larger errors were found for some of the low-angle reflections, for which the intensities were systematically lower than their calculated values by 10–20%; these discrepancies were ascribed to extinction effects. Since the inner reflections are of minor importance in determining the slope of the curve of $\ln [F_c/F_o]$ versus $\sin^2 \theta/\lambda^2$, no attempt was made to correct for these errors.

3. Analysis of results

The measured intensities were corrected for multiplicity, Lorentz and polarization factors, and a set of structure factors on an arbitrary scale was calculated. Values of $\ln [F_c/F_o]$ were then plotted against $\sin^2 \theta/\lambda^2$ and the best straight line through the experimental points was derived by the method of least squares. The values of the atomic scattering factors were obtained from the following sources: Co, Ni and Cu were obtained from Viervöll & Ögrim (1949); these are Hartree f curves. Au values were obtained from Henry (1954); these are the Hartree values for Au^+, but the differences between the f curves of the ion and the atom should be negligible at all except the smallest angles. Pt values were obtained from the *Internationale Tabellen* (1935); these are Thomas–Fermi values.

The Hönl corrections for the K shells of Co, Ni, Cu, Au and Pt were calculated as described by James; the corrections for the L shells for the first three elements are negligible. For Au and Pt there is an appreciable dispersion effect in the L shells for which a satisfactory theoretical treatment is lacking. The corrections were therefore estimated from the experimental results of Brentano & Baxter (1934) for tungsten. Values of $\delta f(\mathrm{Pt})_L = -4{\cdot}0$ and $\delta f(\mathrm{Au})_L = -3{\cdot}5$ were used. The dispersion corrections for Li and Mg are negligible.

4. Results

The value of B derived from the measured intensities are summarized in Table 1. The values of the Debye temperatures derived from the X-ray measurements are given in Table 2, where the values available from elastic-constant measurements (Koster, 1948; Quimby & Sutton, 1953) are also collected. These values have all been corrected to apply to X-ray measurements (Zener & Bilinsky, 1936). The agreement among the different values is good. The mean values of Θ_M were used to calculate the thermal contributions to the experimental Debye factors.

Table 1. *Values of B measured at 295° K. and 90° K. for Cu_3Au, CoPt, NiAu and LiMg*

The values of B are in $Å^{-2}$

	At 295° K.			At 90° K.		
Alloy	B (total)	B (thermal)	B' (distortion)	B (total)	B (thermal)	B' (distortion)
Cu_3Au	0·69	0·52	0·17	0·36	0·19	0·17
CoPt	0·49	0·35	0·14	0·23	0·13	0·10
NiAu	0·99	0·67	0·32	0·78*	0·42*	0·35*
LiMg	1·93	1·60	0·33	1·06	0·66	0·40

* Measured at 180° K.

Table 2. *Values of Debye temperature obtained by various methods*

Values are in °K.

Alloy	Other measurements	Comparison of X-ray intensities at 295° K. and 90° K.
Cu_3Au	271 (1) 268 (2)	268 (3)
CoPt	273 (4)	283 (3)
NiAu	—	254 (3)*
LiMg	—	380 (3)

The references are to the experimental data from which Θ_M was calculated.

(1) Calculated from elastic constants (Goens, Weerts & Stenzel, 1933).

(2) Calculated from Young's modulus (Rohl, 1933).

(3) Present investigation.

(4) Calculated from Young's modulus (Gebhardt & Koster, 1940).

* X-ray intensities at 295° K. and 180° K. compared.

As the results in Table 1 show, the measured values of B are in all instances greater than those calculated from the lattice vibrations alone; for the measurements at low temperatures, the experimental values are almost twice as big as the thermal contributions. This is a definite qualitative proof of the existence of the quasi-temperature effect predicted by the X-ray theories. In the next section we shall examine the quantitative agreement between theory and experiment.

5. Comparison of theory and experiment

The theory of Huang was developed for dilute solutions, and thus applies only roughly to Cu_3Au and not at all to the other alloys. For Cu_3Au the Huang theory gives B' (distortion) $= 0{\cdot}422$ Å², which is about two and one-half times as large as the measured value. This large discrepancy is a consequence of the fact that Cu_3Au cannot be treated as a dilute solution. On the other hand Borie's theory was developed for random solutions of any composition and thus should apply approximately to the Cu_3Au, CoPt and NiAu alloys. (The results for LiMg will be discussed separately below.) For f.c.c. alloys this theory gives

$$B' \text{ (distortion)} = 8{\cdot}43\pi^2 a^2 \frac{m_B}{m_A} (\varepsilon^1_{BB})^2 , \qquad (5)$$

where a is the lattice parameter, m_A, m_B are the atomic fractions of A and B present and

$$\varepsilon^1_{BB} = (r^1_{BB} - r_1)/r_1 \, . \qquad (6)$$

Here r^1_{BB} is the distance between neighboring B atoms and r_1 is the mean nearest-neighbor distance. For a face-centered cubic lattice $r_1 = a/\sqrt{2}$.

For the coefficient governing the size-effect diffuse scattering, Borie obtains

$$\beta_1 = \frac{1}{\eta - 1}\,\varepsilon^1_{BB}\left(1 + \frac{m_B}{m_A}\eta\right) , \qquad (7)$$

where $\eta = f_B/f_A$. This expression is equivalent to that derived by Warren *et al.* (1951) if the short-range order is neglected and if

$$m_A\varepsilon^1_{AA} + m_B\varepsilon^1_{BB} = 0 \, .$$

This latter condition is a consequence of the model used in the analysis, in which the atomic displacements are calculated on the basis that elastic atoms of different sizes are placed on the sites of the average lattice. Since the experimental value of the lattice parameter was used to calculate the average interatomic distance, there can be no overall dilation and the condition above must hold.

Values of ε^1_{BB} can be calculated from the measured values of β_1 (listed in the references cited on the diffuse scattering for these alloys), and used in turn to calculate values of B' (distortion). These calculated values of B' (distortion) are compared with the values measured in the present investigation in Table 3. The agreement between the measured and calculated results is fairly good and provides confirmation of the general correctness of Borie's conclusions. Since the theory has been developed for a completely random solid solution, whereas there is an appreciable degree of short-range order in the three alloys considered here, complete agreement between theory and experiment is not to be expected. Neither the present measurements of B' (distortion) nor the previous measurements of β_1 are sufficiently accurate for any significance to be ascribed to the discrepancies found here between theory and experiment.

Table 3. *Comparison of measured values of B' (distortion) with those calculated from the size-effect diffuse scattering coefficient β_1*

The r.m.s. static displacements are also compared with the r.m.s. dynamic displacements at 295° K. and 90° K.

	B' (distortion)			R.m.s. thermal displacements	
Alloy	Measured (Å^2)	Calculated from β_1 (Å^2)	R.m.s. static displacement (Å)	At 295° K. (Å)	At 90° K. (Å)
Cu_3Au	0·17	0·16	0·08	0·14	0·09
CoPt	0·12	0·09	0·07	0·12	0·07
NiAu	0·32	0·35	0·11	0·16	0·13*
LiMg	0·37	—	0·11	0·25	0·16

* At 180° K.

6. Discussion

The existence of a quasi-temperature effect in the three alloys is strong evidence for the presence of local static displacements in solid solutions when the sizes of the component atoms differ appreciably. Furthermore, the success of the X-ray theory, based on a simple elastic model of the solid-solution lattice, in predicting the magnitude of the distortion contribution to the Debye factor suggests that a model of this kind is a reasonable first approximation to the actual condition of the solid solution.

The present measurements of B' (distortion) support the conclusions drawn previously from diffuse-scattering measurements about atomic sizes in solid solution (Warren *et al.*, 1951; Averbach *et al.*, 1954). Since B' (distortion) depends on the square of the displacement strain ε^1_{BB}, it provides a sensitive way of checking suggested values of atomic sizes. For example, if the atoms in disordered Cu_3Au (where we put $A \equiv$ Cu, $B \equiv$ Au) were to retain the sizes characteristic of the pure metals, then B' (distortion) would be about 3·5 Å^2, whereas a value of 0·17 Å^2 was observed. Clearly there must be considerable relaxation of the atomic sizes towards the average size, and the agreement between observed and calculated values of B' (distortion) shows that the atomic diameters deduced previously from the size-effect diffuse scattering (Averbach *et al.*, 1954) must be close to being correct. Similar considerations apply to the atomic sizes obtained for the Au–Ni system.

The results for LiMg require special comment. There are indications, which are discussed elsewhere (Herbstein & Averbach, 1956), for concluding that the elastic model of solid solutions does not apply to the Li–Mg system and that the displacements of the atoms from the sites of the average lattice are due to a contraction of the Li–Mg interatomic distances with respect to the mean atomic diameter. Nevertheless both the quasi-temperature effect on the Bragg intensities and the size-effect diffuse scattering are found, and these results have been included here to emphasize that both diffraction effects are general consequences of the existence of static displacements from the sites of the average lattice and do not depend on the postulation of a particular model for the solid solution.

The measurement of static displacements in the solid-solution lattice provides a supplementary method of determining atomic sizes in solid solutions. Since the effect of the static displacements on the Bragg intensities does not depend on the difference in the scattering factors of the components, this method provides a direct way of investigating atomic sizes in solid solutions such as Cu–Ni and Cu–Zn, while it is also capable of yielding results for dilute solutions for which the diffuse scattering would be small. It should, however, be noted that the interpretation of the measured values of B' (distortion), and also of β_1, in terms of atomic sizes requires the assumption of a particular model for the solid solution.

It is of interest to compare the magnitudes of the static and dynamic displacements of the atoms from the lattice positions. These are also listed in Table 3. For NiAu r.m.s. static displacement is approximately equal to the r.m.s. thermal vibration amplitude at room temperature, while for the other alloys considered here the dynamic displacements are larger than the static displacements at room temperature. These quantities become approximately equal in magnitude at liquid-nitrogen temperature.

The authors are grateful to the Atomic Energy Commission for their support, and to Prof. B. E. Warren for many stimulating discussions. They would also like to acknowledge the assistance of Roy Kaplow in obtaining the data for the gold–nickel alloy and of Robert Goss in various experimental phases of this program.

References

AVERBACH, B. L., FLINN, P. A. & COHEN, M. (1954). *Acta Metallurg.* **2**, 92.

BORIE, B. S. (1955). Unpublished research.

BRENTANO, J. C. M. & BAXTER, A. (1934). *Z. Phys.* **89**, 720.

COYLE, R. A. & GALE, B. (1955). *Acta Cryst.* **8**, 105.

FLINN, P. A., AVERBACH, B. L. & COHEN, M. (1953). *Acta Metallurg.* **1**, 664.

GEBHARDT, E. & KOSTER, W. (1940). *Z. Metallk.* **32**, 253.

GOENS, E., WEERTS, J. & STENZEL, W. (1933). *Z. Instrum-Kde.* **53**, 242.

HENRY, W. G. (1954). *Acta Cryst.* **7**, 138.

HERBSTEIN, F. H. & AVERBACH, B. L. (1956). *Acta Metallurg.* To be published.

HUANG, K. (1947). *Proc. Roy. Soc.* A, **190**, 102.

Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935), vol. 2. Berlin: Borntraeger.

IVERONOVA, V. I. & KATCNELSON, A. A. (1954). *Dokl. Akad. Nauk, SSSR*, **39**, 391.

IVERONOVA, V. I., KUZMINA, Z. I., FUTERGENDLER, S. I. & DEKLOF, E. I. (1951). *Izv. Akad. Nauk, SSSR, Ser. Fiz.* **15**, 44.

JAMES, R. W. (1948). *The Optical Principles of the Diffraction of X-Rays.* London: Bell.

KOSTER, W. (1948). *Z. Metallk.* **39**, 145.

KURDJUMOV, G. V., ILINA, V. A., KRITSKAYA, V. K. & LYSAK, L. I. (1953). *Izv. Akad. Nauk. SSSR*, **17**, 217.

LONSDALE, K. (1948). *Acta Cryst.* **1**, 142.

QUIMBY, S. L. & SUTTON, P. M. (1953). *Phys. Rev.* **91**, 1122.

ROHL, H. (1933). *Ann. Phys., Lpz.* (5), **18**, 155.

RUDMAN, P. S. (1955). ScD. Thesis, Department of Metallurgy, M. I. T.

VIERVOLL, H. & ÖGRIM, O. (1949). *Acta Cryst.* **2**, 277.

WARREN, B. E., AVERBACH, B. L. & ROBERTS, B. W. (1951). *J. Appl. Phys.* **22**, 1493.

ZENER, C. & BILINSKY, S. (1936). *Phys. Rev.* **50**, 101.

Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.

Acta Cryst. (1956). **9**, 471

Structure et valences de $VCeO_4$.

Par A. DURIF, *Laboratoire d'Électrostatique et de Physique du Métal, Institut Fourier, Grenoble, France*

(*Reçu le* 10 *février* 1956)

Le composé $VCeO_4$ a été préparé par oxydation de $VCeO_3$ obtenu par Bertaut & Forrat (1956). Son diagramme Debye–Scherrer est caractéristique d'un composé quadratique du type zircon:

$$a = 7\cdot39,\ c = 6\cdot50\ \text{Å};\ Z = 4;$$
$$U = 355\ \text{Å}^3;\ D_X = 4\cdot74;\ I4/amd\text{–}D_{4h}^{19};$$

avec

$$4\,\text{Ce en } 4(a),\ 4\,\text{V en } 4(b),\ 16\,\text{O en } 16(h)\,.$$

Dans ce composé Ce est trivalent et V pentavalent. En effet il se rattache à la série des vanadates des terres rares étudiée par Milligan, Watt & Rachford (1949). Dans cette série le volume de la maille croît régulièrement en fonction du rayon ionique du métal de la terre rare. Le volume observé de la maille de $VCeO_4$ (355 Å^3) permet de conclure que dans ce composé Ce doit avoir un rayon ionique supérieur à celui de Pr^{3+} (1·16 Å) car U ($VPrO_4$) = 341 Å^3. Il ne peut donc s'agir que de Ce trivalent (1·18 Å).

Références

BERTAUT, F. & FORRAT, F. (1956). *J. Phys. Radium.* Sous presse.

MILLIGAN, W. O., WATT, L. M. & RACHFORD, H. H. (1949). *J. Phys. Coll. Chem.* **53**, 227.