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Integrated X-ray Intensity Measurements from a Solid Solution of Copper–Gold

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In a solid solution random displacements of the solute and solvent ions from the mean crystal lattice are produced by the elastic strains associated with their different sizes.

A prediction of the effects on the X-ray spectrum is based on a model which treats the solute ions as centres of dilation in a finite isotropic elastic continuum. The resultant theory shows that the addition of solute atoms produces a mean lattice parameter change upon which are superimposed random displacements of the ions. These displacements result in a decrease in the integrated X-ray intensities of the high-order diffraction lines of the form associated with thermal vibrations. The effect is particularly marked in the copper–gold solid solution and comparison of the measured X-ray intensities from copper and a 15 atomic % solution of gold in copper enable one to deduce a value for the root mean square displacement $\sqrt{(\bar{u}^2)}$ due to distortion, when that due to thermal vibration has been allowed for.

Measurements of the X-ray spectra were made using a Geiger-counter spectrometer from which it is deduced that $\sqrt{(\bar{u}^2)} = 0{\cdot}11$ Å. This value compares favourably with the value predicted from the elasticity theory, namely $\sqrt{(\bar{u}^2)} = 0{\cdot}13$ Å.

1. Introduction

The X-ray diffraction spectrum from a crystal containing two kinds of atoms depends on the respective scattering factors and the degree of order. Recent work, for example by Cowley (1950) and Flinn, Averbach & Cohen (1953), has demonstrated convincingly the power of the low-angle-scattering technique in discovering the local atomic arrangements in metallic solid solutions. Information of a more restricted, though similar, nature can also be obtained from a measurement of the integrated intensities of high-order diffraction lines.

A theoretical discussion of the problem of elastic distortion in a solid solution has been given by Huang (1947) and he predicts a diminution of the integrated intensities analogous to that produced by temperature vibrations. This is contrary to the treatment given by Warren, Averbach & Roberts (1951), which predicts no such diminution. The discrepancy lies in the respective assumptions made concerning the atomic displacements from the lattice sites. In the former theory the displacements from any one solute atom are assumed to be spherically symmetric; whereas in the latter they are related to the degree of order and hence depend anisotropically on the identity of the atoms displaced. Detailed analysis shows that the first non-zero components of the intensity modification formulae calculated from these ideas represent, respectively, diminished integrated intensities and diffuse scattering. However, if in the theory of Warren *et al.* (1951) second-order terms are considered then the integrated intensities are diminished; though in this case their detailed computation is rendered prohibitively difficult by the random anisotropy involved in the elastic problem. On the other hand the simpler assumptions of Huang, though physically less realistic, do lead to a tractable elastic problem which might be expected to be a useful guide in estimating the effective atomic sizes in a random solid solution. With these restrictions in mind, a slightly modified and considerably abbreviated version of Huang's theory is given below.

In this elastic sphere model of a dilute solid solution each solute atom is considered to be a centre of distortion in a continuum formed of all the other atoms. As a first approximation the mutual influence of these centres can be considered zero, so that the distortion of the continuum can be described by a simple superposition of them. Thus if $\mathbf{u}(r)$ represents the elastic displacement at a point r under the influence of a single distortion centre at the origin, then the displacement of an atom at a lattice site $\mathbf{a}_n$ due to the elastic fields of all the solute atoms is given by

$$\mathbf{u}_n = \sum_i \mathbf{u}(\mathbf{a}_n - \mathbf{a}_i)\,,$$

where $\mathbf{a}_i$ represents a lattice site occupied by a solute atom. The assumption of elastic isotropy leads to a unique choice of $\mathbf{u}(r)$, for the only suitable spherically symmetrical solution of the elasticity equations is

$$\mathbf{u}(r) = cr/|r|^3,$$

c being a constant. This expression strictly applies to an infinite body, and leads to a non-zero stress at the surface of a finite one. The additional 'image displacement' necessary to ensure that this stress vanishes is considered to be negligible in Huang's paper; but, as Eshelby (1954) has pointed out, its effect is in many problems appreciable and, for example, accounts for about 40% of the volume change in a solid solution.

In the formulae deduced for the lattice parameter and integrated X-ray intensities the effect is embodied in the insertion of a factor γ, where

$$\gamma = 1+\tfrac{4}{3}GK\,,$$

G being the modulus of rigidity and K the compressibility.

If now extinction is ignored the intensity of X-rays scattered by the solid solution crystal is proportional to the mean value of

$$\sum_n\sum_m \exp\,\{2\pi i\mathbf{b}(\mathbf{a}_n-\mathbf{a}_m+\mathbf{u}_n-\mathbf{u}_m)\}$$

summed over all pairs of lattice sites $\mathbf{a}_n$ and $\mathbf{a}_m$, where $\mathbf{b}$ is the reciprocal-lattice vector of the X-ray reflexion considered. This summation is averaged for all possible distributions of the atoms and is then suitably weighted with respect to the scattering-factor products. Inserting the appropriate formulae for $\mathbf{u}_n$ and $\mathbf{u}_m$ and performing the necessary summations, Huang shows that the intensity formula exhibits three separate phenomena: diffuse scattering, a change in lattice parameter and a diminution of integrated intensity. The first of these is not of immediate interest in this paper and will not be considered further. The second expresses the solid-solution parameter as a function of the solute concentration P, i.e.

$$\frac{d-d_0}{d_0}\equiv\frac{\Delta d}{d_0}=\frac{16\pi cP\gamma}{3d^3}\,, \tag{1}$$

where d_0 and d are respectively the parameters of the solvent and the solution. Finally, the third takes the form of an exponential diminution of the integrated intensities as the diffraction angle increases, so that, apart from experimental numerical factors, they are represented by

$$[(1-P)f_T(A)+Pf_T(B)]^2 \exp\left[-\frac{16\pi^2}{3}\bar{u}^2\left(\frac{\sin\theta}{\lambda}\right)^2\right]. \tag{2}$$

Here $f_T(A)$ and $f_T(B)$ are the scattering factors of atoms of types A and B corrected for dispersion and the thermal vibrations. $\bar{u}^2$ is the mean square displacement of the atoms from the lattice sites of the solid solution and is related to the elastic coefficient c, the concentration P and the solution parameter d by the formula

$$\bar{u}^2=\frac{101\cdot 1}{d^4}P(1-P)c^2\gamma^2\,, \tag{3}$$

the numerical factor arising in the various lattice series appearing in the intensity formula. Thus by eliminating c between (1) and (3) a value for $\bar{u}^2$ can be computed from the solution lattice parameter and concentration which, by comparison with the measured value obtained from equation (2), is a measure of the validity of the theory. This value,

$$\bar{u}^2 = 0\cdot 360\frac{1-P}{P}\frac{(d\Delta d)^2}{(d_0)^2}\,, \tag{4}$$

is seen to be dependent on the value of Δd for a given concentration; so that to measure the effect with any precision it is necessary to choose an alloy with a large value of $(\Delta d/P)$, and for this reason a solid solution of gold in copper was used. To measure $\bar{u}^2$ with any degree of accuracy requires a number of high-order diffraction lines, so that molybdenum radiation was used. This has the further advantages of producing comparatively small dispersion and extinction effects.

2. Experimental details

(i) *Apparatus*

The integrated intensity measurements in connection with this solid-solution problem were made on the Geiger-counter spectrometer described by Coyle, Hale & Wainwright (1953). Schematic representations of the optical and electronic arrangements are shown in Figs. 1 and 2.

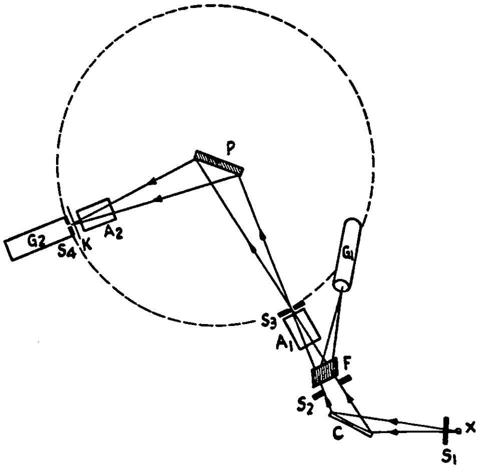

Fig. 1. Layout of spectrometer components.

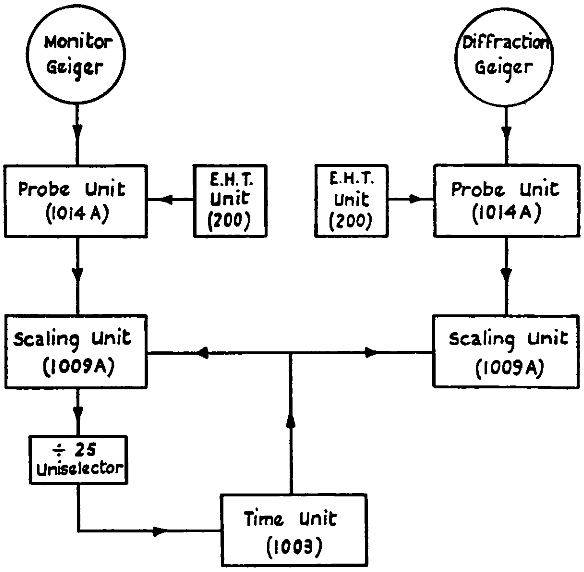

Fig. 2. Schematic diagram of electrical circuits.

Referring to Fig. 1; a diverging beam of X-rays, defined by the 'side on' focus X of a sealed-off tube and the slit S_1, is reflected from a curved quartz crystal C. The subsequent converging beam then passes successively through a slit S_2, placed to reduce extraneous scatter, an aluminium foil F, set to deflect a small proportion of the main beam into the monitor Geiger counter G_1, and a Soller slit system A_1 designed to reduce the vertical divergence of the X-ray beam. An adjustable slit S_3 is placed at the position where the beam has minimum width; this, apart from reducing the extraneous scatter still further, has also, in special circumstances, been used to eliminate either one of the components of the α-doublet. Thus S_3 is the virtual source of a monochromatic beam of 2–3° horizontal aperture falling on the powder block P, which is rotated continually in its own plane. The rotation of the specimen about the spectrometer axis is coupled to that of the Geiger counter G_2 through a half-speed drive, which, after initial setting, enables the geometrical conditions of the Brentano (1937) focusing technique to be satisfied. After diffraction by the powder block, the X-ray beam converges through a second set of Soller slits A_2 on to the slit S_4. A reduction by a factor of about 70:1 in the ratio of fluorescent to diffracted radiation from the powder block is obtained by inserting an aluminium foil K in front of the slit S_4.

The counting circuits (Fig. 2) consist of standard A.E.R.E. units. By this arrangement, when the monitor counter receives a predetermined number of pulses, up to 250,000, both scaling units are switched off and the diffraction count and time are recorded. Thus fluctuations in the X-ray source are compensated and the probe paralysis time corrections can be computed.

(ii) *Preparation of specimens*

The present work was done with two materials supplied by Johnson and Matthey; one a copper–gold solid solution containing 15·58% of 99·98% purity gold, and the other copper of 99·99% purity. Specimens were made of filed particles, about 30 microns in size, pressed into flat discs 1·4 cm. in diameter and 0·15 cm. thick. The pressure used, 13 kg.mm.$^{-2}$, was chosen after measuring the effects of preferred orientation in a number of specimens subject to pressures in the range 5–20 kg.mm.$^{-2}$. For this pressure the specimens cohered well and the X-ray intensity deviations were less than the estimated experimental scatter. The specimens were annealed for about 5 hr. at 500° C., sufficient to give sharp spots on back-reflexion Debye rings. Part of each specimen was used to make a measurement of the crystal cell parameter using a calibrated 9 cm. powder camera. The values obtained were:

$$\text{Cu: } a\ (20^\circ\ \text{C.}) = 3{\cdot}6152 \pm 0{\cdot}0001\ \text{Å}$$
$$\text{Cu–Au: } a\ (20^\circ\ \text{C.}) = 3{\cdot}7070 \pm 0{\cdot}0001\ \text{Å}$$

(iii) *Counting technique*

The measurement of the integrated intensities was made easier and more accurate than numerical integration of a measured diffraction line profile by use of non-overlapping counting sequences with a wide Geiger-counter slit in 6 or 7 positions. With a slit width of 38′ the main effective intensity of the line is measured at one position of the slit, and any overlap errors are at a minimum since the slit edges are at points of low intensity. Furthermore, since the background count, now much greater than cosmic, is increased, the statistical accuracy of the measured integrated intensity is greatly improved. All the counts were corrected for paralysis time according to the formula

$$N = N_0/(1-N_0KT) \qquad \text{(Arndt, 1949)},$$

where N is the corrected counting rate, N_0 is the recorded counting rate, T is the paralysis time, and K is the mean square intensity of source/(mean intensity of source)^2. For Mo $K\alpha$ radiation generated at 50 kV., full-wave rectified, and 20 mA., the appropriate value of K, obtained by numerical integration, is 2·30.

The integrated intensity of any one line is then computed from the difference between the count registered with the slit straddling the line and the background count, as estimated from the arithmetic mean of the other slit positions in the sequence. Thus if the counts at the positions 1, 2, ..., $2n+1$ are $N_1, N_2, \ldots, N_{2n+1}$, N_{n+1} being the line count, the integrated intensity is estimated as

$$I = N_{n+1} - \frac{1}{2n}\left(\frac{M}{M'}\right) \sum_{i \neq n+1}^{2n+1} N_i\,,$$

where M and M' are the respective monitor counts of the line position and the background positions. The accuracy of the measurement is then proportional to the square root of the sum of the variances of the terms in the above formula, which is given by

$$\sigma^2(I) \approx N_{n+1}(1+N_{n+1}/M) + \frac{1}{4n^2}\left(\frac{M}{M'}\right)^2 \sum_{i \neq n+1}^{2n+1} + N_i(1+N_i/M');$$

whence the percentage probable error is given by

$$\varepsilon \approx 67{\cdot}5\ \sigma(I)/I\,\%\,.$$

To make the best use of the method a chart record of the spectrum is made to give the positions and intensities of the lines, whence, using the formula for the error given above, the most economical count sequence can be estimated.

In using molybdenum radiation it was not found possible, with the monochromator crystal available, to eliminate the α_2 component. Thus at high diffraction angles the diffraction line pair will not lie within one slit width and counting times must necessarily be increased to obtain comparable accuracy with that obtainable using fully monochromatised radiation.

The nature of the problem requires that only the relative integrated intensities of the lines need be measured. Thus to correct for any changes in experimental conditions, constant reference counts on one diffraction line were made and all the other integrated intensities were normalized with respect to it.

3. Experimental results

The experimental test of the effects of distortion on the integrated X-ray intensities from the copper–gold solid solution is divided into two parts. In view of the numerous other factors involved in the computation of intensities, a detailed comparison of the experimentally determined and theoretically computed intensities for copper was first carried out. This was done primarily to check the experimental procedure, but it also served to check the assumptions made in connection with the atomic scattering factors.

If it is assumed that there is no extinction, the integrated intensity of a diffraction line with indices (hkl) from a thick powder slab irradiated by an incident intensity I_0 is given by

$$I(hkl) = I_0 q |F(hkl)|^2 G(\theta, \alpha) A \ ,$$

where q is the multiplicity of the crystal planes contributing to the diffraction ring and $F(hkl)$ is the scattering factor of a lattice cell. $G(\theta, \alpha)$ is defined by

$$G(\theta, \alpha) \equiv \frac{1+\cos^2 2\theta \cos^2 2\alpha}{\sin^2\theta \cos\theta (1+\cos^2 2\alpha)} \ ,$$

where θ and α are the Bragg angles for diffraction from the monochromator; the function expresses the effects of polarization and the spectrometer geometry. The factor A is defined by

$$A \equiv \frac{l}{32r} \frac{N^2\lambda^3}{\pi\mu} \left(\frac{e^2}{mc^2}\right)^2 ,$$

where l is the length of the receiving slit of the Geiger counter G_2 (Fig. 1), r is the radius of the 'Brentano' focusing circle, N is the number of crystal lattice cells in unit volume, λ is the wavelength of the incident X-radiation, μ is the effective linear absorption coefficient of the specimen and e, m and c are respectively the charge of an electron, the mass of an electron and the velocity of light. Now, since only the relative intensities of the lines from any one specimen are required, agreement between theory and experiment can be tested in terms of the ratio of the measured and computed intensities; thus the factor A need not be computed and the essential information is contained in the function $K(hkl)$ defined by the relation:

$$K(hkl) = E(hkl)/C(hkl) \ ,$$

where $E(hkl)$ is the normalized intensity count, and

$$C(hkl) = q|F(hkl)|^2 G(\theta, \alpha) \ .$$

The polarization factor $G(\theta, \alpha)$ is readily computed; as also is the multiplicity q if there is no preferred orientation in the specimen. In the specimens used any variations in q due to this latter cause appear to be of the same order of magnitude as the estimated probable errors in the values of $E(hkl)$, so that values of q appropriate to a randomly orientated powder can be assumed in all the subsequent computations. The calculation of the scattering factors for the copper and copper–gold specimens, however, requires different and more detailed consideration.

Copper scattering factors

In copper the scattering factors used were those corresponding to scattering by stationary atoms of X-rays of a wavelength short in comparison with the copper absorption-edge wavelength, as computed from the Hartree distribution of a singly ionized copper atom by James & Brindley (1931). These values must be corrected to take into account the proximity of the X-ray wavelength to the absorption edge of the specimen and its mechanical vibration spectrum.

The dispersion correction is small with molybdenum radiation and can be computed with sufficient accuracy from Hönl's theory (James, 1948). If f_0 is the uncorrected scattering factor, that corrected for dispersion by the K electrons is given by

$$|f| \approx f_0 + \Delta f'_k + \tfrac{1}{2}(\Delta f''_k)^2/(f_0 + \Delta f'_k) \ .$$

Values of f'_k and f''_k corresponding to different scattering atoms and incident wavelengths are tabulated in James's book and the appropriate corrections for copper and gold atoms scattering molybdenum radiation are:

$$\text{Cu:} \quad |f| \approx f_0 + 0{\cdot}26 + 0{\cdot}58/(f_0 + 0{\cdot}26) \ ,$$
$$\text{Au:} \quad |f| \approx f_0 - 1{\cdot}06 \ .$$

That the form of this correction is substantially correct has been verified experimentally by Brindley (1936), who, in the same paper, substantiates the James & Brindley (1931) computations.

The temperature correction to the copper scattering factors is based on the Debye–Waller theory of lattice vibrations. On this basis the appropriate value for the scattering factor for a monatomic cubic crystal is given by

$$f_T = |f| \exp\left\{-\frac{8}{3}\pi^2 \bar{u}^2 \left(\frac{\sin\theta}{\lambda}\right)^2\right\} ,$$

where $\bar{u}^2$ is the mean square displacement of an atom from its average position in the crystal. The value of $\bar{u}^2$ can be expressed as a function of a slightly modified Debye characteristic temperature as derived from specific heat measurements:

$$\bar{u}^2 = \frac{4{\cdot}364 \times 10^{-14} T}{A\Theta^2} \{\varphi(x) + \tfrac{1}{4}x\} \ , \tag{5}$$

where A is the atomic weight, Θ the Debye temperature, T the absolute temperature of the specimen,

Table 1

	Cu						Cu+15 % Au				
hkl	f_T^2	$C(hkl)$	$E(hkl)$	ε	$K(hkl)$ Cu$^+$	$K(hkl)$ Cu	f_T^2	$C(hkl)$	$E(hkl)$	ε	$K(hkl)$
111	447	$2{\cdot}32\times10^{5}$	$1{\cdot}81\times10^{5}$	0·2	0·780	0·900	757	$4{\cdot}15\times10^{5}$	$1{\cdot}58\times10^{5}$	0·3	0·381
200	384	$1{\cdot}11\times10^{5}$	$1{\cdot}03\times10^{5}$	0·3	0·928	1·081	660	$2{\cdot}01\times10^{5}$	$8{\cdot}26\times10^{4}$	0·3	0·411
220	229	$6{\cdot}25\times10^{4}$	$5{\cdot}82\times10^{4}$	0·3	0·931	1·018	419	$1{\cdot}21\times10^{5}$	$5{\cdot}73\times10^{4}$	0·3	0·474
311	169	$6{\cdot}46\times10^{4}$	$6{\cdot}09\times10^{4}$	0·3	0·943	0·958	323	$1{\cdot}31\times10^{5}$	$5{\cdot}96\times10^{4}$	0·3	0·455
222	152	$1{\cdot}75\times10^{4}$	$1{\cdot}62\times10^{4}$	0·7	0·926	0·914	296	$3{\cdot}61\times10^{4}$	$1{\cdot}63\times10^{4}$	0·7	0·452
400	110	$6{\cdot}80\times10^{3}$	$6{\cdot}29\times10^{3}$	1·5	0·93	0·86	223	$1{\cdot}46\times10^{4}$	$6{\cdot}00\times10^{3}$	1·5	0·411
331	90·5	$1{\cdot}82\times10^{4}$	$1{\cdot}68\times10^{4}$	1·5	0·92	0·85	184	$3{\cdot}93\times10^{4}$	$1{\cdot}59\times10^{4}$	1·5	0·404
420	84·1	$1{\cdot}59\times10^{4}$	$1{\cdot}45\times10^{4}$	2	0·91	0·83	175	$3{\cdot}51\times10^{4}$	$1{\cdot}43\times10^{4}$	1·5	0·407
422	65·7	$9{\cdot}94\times10^{3}$	$8{\cdot}93\times10^{3}$	2	0·90	0·82	140	$2{\cdot}25\times10^{4}$	$8{\cdot}83\times10^{3}$	2	0·392
333 511	56·0	$9{\cdot}79\times10^{3}$	$8{\cdot}96\times10^{3}$	2	0·92	0·83	119	$2{\cdot}21\times10^{4}$	$8{\cdot}33\times10^{3}$	2	0·377
531	35·9	$6{\cdot}92\times10^{3}$	$6{\cdot}21\times10^{3}$	3	0·90	0·77	79·5	$1{\cdot}62\times10^{4}$	$5{\cdot}58\times10^{3}$	3	0·344
442 600	34·4	$4{\cdot}02\times10^{3}$	$3{\cdot}84\times10^{3}$	4	0·96	0·82	76·2	$9{\cdot}41\times10^{3}$	$3{\cdot}03\times10^{3}$	6	0·32
620	28·8	$2{\cdot}41\times10^{3}$	$2{\cdot}34\times10^{3}$	7	0·97	0·82	64·4	$5{\cdot}67\times10^{3}$	$1{\cdot}81\times10^{3}$	12	0·32
553 731	14·7	$2{\cdot}88\times10^{3}$	$2{\cdot}75\times10^{3}$	6	0·95	0·87	31·5	$6{\cdot}23\times10^{3}$	$1{\cdot}80\times10^{3}$	12	0·29

x is $\Theta/(T)$ and $\varphi(x)$ is the tabulated Debye function. It is often assumed that the appropriate value of the Debye temperature to insert in the above formula should be identical with the specific heat value (Owen & Williams, 1947). Such agreement is neither justified theoretically, nor from the measured values of $K(hkl)$ for copper would it seem to be justified experimentally. For, as Zener & Biljinsky (1936) have pointed out, the mean-value definitions of the Debye temperatures in the specific-heat and lattice-vibration theories are different. If Θ_D and Θ_M are respectively these values, then they are related by a function of the Poisson ratio σ:

$$\Theta_M = f(\sigma)\Theta_D\,.$$

For copper the computed value for $f(\sigma)$ is 1·029, so that, using the room-temperature value of 315° K. for Θ_D (Seitz, 1940), the value of Θ_M to be used in the expression for $\bar{u}^2$ is 324° K., whence the variation of the copper scattering factors with Bragg angle is given by

$$f_T = |f|\exp\{-0{\cdot}522\sin^2\theta/\lambda^2\}\,.$$

Values of q, $G(\theta,\alpha)$, f_T^2 and $C(hkl)$ are shown in Table 1, together with the normalized measured intensities $E(hkl)$ of the corresponding lines. The value of $K(hkl)$ for the first line is small, owing to extinction, but thereafter the values are constant within statistical error. Thus the experimental and theoretical procedures appear justified and can be extended with confidence to the analysis of the powder diffraction pattern of a copper–gold solid solution. In the last column of the table the values of $K(hkl)$, as computed using scattering factors for the unionized copper atom are seen not to be constant.

Copper–gold scattering factors

As shown in § 1, the scattering factor of the composite crystal can be written as the product of two factors, one being the scattering factor of an undistorted random solid solution and the other representing the effect of interionic forces on the positions of the scattering units. The magnitude of the latter factor is the subject of this investigation so that it is necessary that the former should be independently estimated.

The main difficulty in making this computation is the estimation of the lattice-vibration correction. This cannot strictly be done by multiplying the zero-temperature composite scattering factor by an exponential function of the form used in copper, since this would imply that all the atoms vibrated with the same amplitude. In general this is not so, for the thermal vibrations depend on the environment and inertia of each atom. Formally in an ordered structure the mean square vibration of each kind of atom in the unit cell should be considered separately, so that the structure factor can be written as

$$F(\mathbf{b}) = \sum_j f(\mathbf{x}_j)\exp\left\{2\pi i\mathbf{b}\mathbf{x}_j - \frac{8\pi^2}{3}\bar{u}_j^2\frac{\sin^2\theta}{\lambda^2}\right\}$$

summed over the atom sites in a unit cell. In this formula $\bar{u}_j^2$ is the mean square displacement of atoms with atomic co-ordinations $\mathbf{x}_j$; and $\mathbf{b}$ is the reciprocal-lattice vector of the spectrum. Even in this case the computation of the values of $\bar{u}_j^2$ is difficult and, as a comparison of the theoretical and experimental estimates of their magnitudes in a number of alkali-halides shows (Lonsdale, 1948), is inaccurate. In a disordered structure a detailed computation would be even more difficult, so that it is necessary to resort to some suitable average for the vibration amplitudes. The Debye temperature can be computed from the elastic constants (James, 1948) and the values are in quite good agreement with the modified specific-heat values: for example, the values for copper and gold are respectively 339° K. and 177° K., compared with the corresponding modified specific-heat values of

324° K. and 177° K. Similarily, one can compute the appropriate Debye temperature from the elastic constants of the copper–gold solid solution. Experimental values of these constants were not known, but from an elastic theory of solid solutions (Pines, 1940) they can be computed with sufficient accuracy. The Debye temperature was deduced to be 283° K., from which a value of the root-mean-square displacement can be calculated from formula (5), using the mean atomic weight given by

$$M(\text{Cu Au}) = PM(\text{Au})+(1-P)M(\text{Cu})\,.$$

The resultant value, $\sqrt{(\bar{u}^2)} = 0{\cdot}139$ Å, is given approximately by the formula

$$\bar{u}^2(\text{Cu Au}) = (1-P)\bar{u}^2(\text{Cu})+P\bar{u}^2(\text{Au})\,,$$

where $\sqrt{(\bar{u}^2)}(\text{Cu}) = 0{\cdot}136$ Å and $\sqrt{(\bar{u}^2)}(\text{Au}) = 0{\cdot}145$ Å have been computed from the elastic constants of copper and gold. Thus on this basis it is considered reasonable to use the value $\sqrt{(\bar{u}^2)} = 0{\cdot}142$ Å obtained when those for copper and gold, as evaluated from the more reliable specific-heat data (i.e. $\sqrt{(\bar{u}^2)}(\text{Cu}) = 0{\cdot}141$ Å and $\sqrt{(\bar{u}^2)}(\text{Au}) = 0{\cdot}145$) are inserted in the above formula. The variation of the copper–gold scattering factors with Bragg angle are thence given by

$$f_T = \{(1-P)|f(\text{Cu})|+P|f(\text{Au})|\}\exp\{-0{\cdot}531(\sin\theta/\lambda)^2\}\,.$$

The values of f_T^2, $C(hkl)$ etc. are tabulated, as for copper, in Table 1.

For the copper scattering factors the values in the previous section were used; for the gold the values computed by Henry (1953), for scattering of short wavelengths from the Hartree distribution of a singly ionized atom, were used.

In this case the values of $K(hkl)$ are not constant, but show a monotonic decline as $\sin\theta/\lambda$ increases. The intensity measurements for the high-order reflexions are not sufficiently accurate to discriminate in favour of any particular functional relationship between $K(hkl)$ and $\sin\theta/\lambda$. Instead, assuming that the predicted exponential form of the elastic distortion intensity term is correct, it is then possible to deduce a value for the corresponding root-mean-square displacement of the atoms from their lattice sites. From the theory outlined in § 1 the computed intensity $C'(hkl)$ is given by

$$C'(hkl) = C(hkl)\exp\left\{-\frac{16\pi^2}{3}\bar{u}^2\frac{\sin^2\theta}{\lambda^2}\right\},$$

whence

$$\ln[K(hkl)] = \text{const.} - \frac{16\pi^2}{3}\bar{u}^2\frac{(\sin\theta)^2}{\lambda^2}\,.$$

The value for $\sqrt{(\bar{u}^2)}$ can then be determined from the slope of the straight line, which, from the method of least squares, is calculated to fit the points with coordinates $(\sin\theta/\lambda)^2$ and $K(hkl)$. The scatter of these points is shown in Fig. 3 and the probable value for the line slope is calculated from the least-squares method. Thus the root-mean-square displacement due to the elastic distortion is measured to be

$$\sqrt{(\bar{u}^2)} = 0{\cdot}112\pm0{\cdot}001\ \text{Å}\,.$$

These limits of error express only the scatter in the experimental results and do not include any measure of the uncertainty in the theoretical scattering factors or in the computed thermal vibrations. The agreement between the measured and computed intensities for the copper specimen is good to within 1 %, so that confidence can be placed in both the experimental technique and the temperature-corrected ionized copper scattering factors. Further, taking Henry's estimation of the computational errors in the ionized gold scattering factors into account, their contribution to the coppper–gold integrated intensities should make the overall inaccuracy due to scattering factors of the order of 2 %. Thus the major inaccuracy is in the thermal vibration corrections of the composite lattice, for these may well be as much as 10 %.

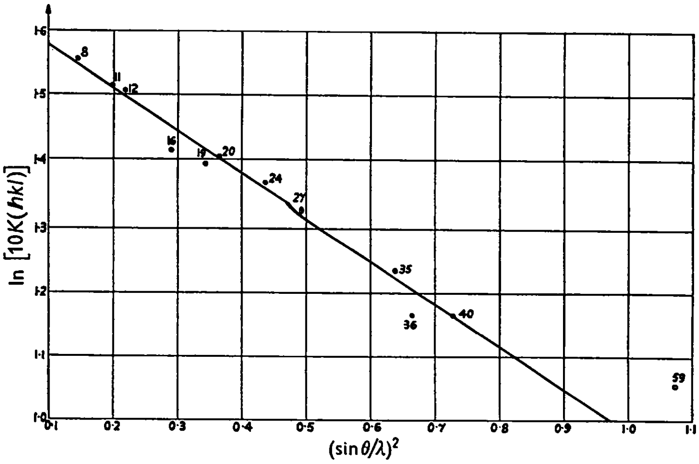

Fig. 3. Graph showing the ratio of the measured integrated intensities and those computed without any assumed lattice distortion as a function of $\sin\theta/\lambda$ for a 15 % solution of gold in copper.

4. Discussion

A value for the root-mean-square displacement of the atoms in the solid solution due to elastic distortion can also be computed from (4); using the measured values of the concentration and lattice parameter it is $\sqrt{(\bar{u}^2)} = 0{\cdot}132$ Å.

In view of the possible sources of error mentioned previously, this value is in good agreement with the experimental value. However, it does not necessarily follow that the elasticity theory is fully established, for, as was pointed out in the first section, it is based on certain unrealistic assumptions. The assumption of spherically symmetrical elastic displacements is not consistent with the markedly anisotropic elastic constants of both copper and gold. The assumption that the atoms are randomly distributed is not supported by diffuse-scattering measurements made on a 23% alloy (Sutcliffe & Jaumot, 1953), though it does not appear to be far wrong. Furthermore, there is some evidence from parameter measurements, not only in the Cu–Au system (van Arkel & Basart, 1928) but also in the systems Cu–Zn, Cu–Ga, Cu–Ge and Cu–As (Hume-Rothery, Lewin & Reynolds, 1936), that the values of c so calculated decrease with the solute concentration. Such an effect would be directly associated with an interaction between the solute-atom distortion centres, which in the theory is assumed to be negligible. The magnitude of the effects of all these assumptions on the magnitude and meaning of c is difficult to estimate. If, however, on the basis of the agreement between the two values for $\sqrt{(\bar{u}^2)}$, it is assumed that they affect the value of c by only 10% then its value is $c = 0{\cdot}33 \pm 0{\cdot}3$.

In the elasticity theory the strain field about the solute atom is identical with that round a spherical inclusion, initially of radius r_B, set into a spherical cavity of radius r_A. However, two extremum values of c can be obtained, depending on whether one assumes the solute inclusion to have a zero compressibility or that of the parent lattice:

(i) Incompressible solute sphere:

$$c = r_A^2(r_B - r_A) = 0{\cdot}27$$

on inserting values of r_A and r_B equal to half the distance of nearest approach in the parent lattices.

(ii) Compressible solute sphere (Pines, 1940):

$$c = \frac{r_A^2(r_B - r_A)}{1+\frac{4}{3}G(A)K(B)} = 0{\cdot}20\,.$$

Thus it would appear that the gold solute atoms behave approximately as incompressible spheres. However, it must be borne in mind that the associated value of c is slightly exaggerated, for the solute atom is effectively constrained and cannot take advantage of the larger cavity radius in directions other than nearest-neighbour vectors.

It is interesting to consider also a solid solution of aluminium in copper. The work described above indicates that one can derive a value for c solely from parameter measurements. For a 15 atomic% solution the value is computed to be $c = 0{\cdot}16$. Again using the two elastic models as above, the appropriate values of c are

$$\text{(i) } c = 0{\cdot}25, \quad \text{(ii) } c = 0{\cdot}14\,.$$

Thus in this case the aluminium solute atoms behave more nearly as compressible spheres. It is therefore evident that the local 'elastic' distortion associated with any solute atom is not solely given by the difference in 'size' of the solute and solvent atoms but also depends on the relative deformabilities, which are not directly related to the bulk elastic constants.

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