

4 Ga₂S₃ molecules would be required per unit cell giving a calculated density of 3.64 g.cm.⁻³. This agrees well with the measured macroscopic density of 3.65 g.cm.⁻³ given in *Handbook of Chemistry and Physics* (1957-58). Although the symmetry of the space group *C*2 would be satisfied by this disposition of sulphur atoms, this would not be so for the tetrahedral positions in which the gallium atoms might be supposed to lie. It appears then that the structure of α -Ga₂S₃ is not related to the wurtzite structure. On the other hand, the space-group requirements would permit the gallium atoms to be octahedrally co-ordinated, but this

possibility must remain tentative until the full structure analysis has been completed.

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The Effect of Temperature on Local Order Diffuse Scattering from Alloys. I*

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The theory of the diffuse scattering of X-rays from binary alloys with local order has been extended to include explicitly the effects of thermal vibrations. By adopting certain simplifying assumptions about the lattice vibrations it is found that the thermal effects can be expressed in the form of appropriate Debye-Waller factors modifying the usual diffuse scattering terms. Experimental measurements verify the predicted general nature and magnitude of the temperature effect. Neglect of this effect appears to be a significant source of error in past experimental determinations of local order in alloys.

Introduction

Diffraction theory describing the diffuse X-ray scattering arising from local ordering† of the atoms in a binary alloy has been extended to include the modifying effects of static displacements due to differing atomic sizes by several authors [see, for example, Huang (1947); Warren, Averbach & Roberts (1951); Borie (1957), (1959)], but the analogous extension to include the effects of the dynamic displacements due to thermal vibrations has received relatively little attention. Muldawer (1954) attempted to develop a scattering theory in which the lattice vibrations were explicitly included, but his theory was not carried beyond a first formal step. Münster & Sagel (1957) developed a theory of the local order diffuse scattering in powder patterns in terms of continuous interatomic pair probability density functions, thus including thermal displacements implicitly; these continuous

probability functions were then to be determined from each experiment.

We give here an approximate theory of local order diffuse X-ray scattering in which the modifying effects of the thermal vibrations are explicitly described. The theory is limited to binary alloys with only short range atomic correlations, and for simplicity it is further restricted to alloys with monatomic face-centered or body-centered cubic lattices. In this paper we develop the theory in detail for alloys with no atomic size effects and demonstrate the nature and magnitude of the predicted temperature effects with calculated examples and experimental measurements. The extension of the theory to alloys with size-effect static displacements following the model of Borie (1957) is given in a following paper.

Theory

The intensity of X-rays scattered by an array of atoms, neglecting extinction and absorption, is given in electron units as

$$I = \sum_m \sum_n f_m f_n \exp [i\mathbf{K} \cdot (\mathbf{r}_m - \mathbf{r}_n)], \quad (1)$$

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† The term local order is taken to include both the conventional type of short range order and the clustering of like atoms preceding precipitation.

where f_m and f_n are the scattering factors of atoms located by vectors \mathbf{r}_m and \mathbf{r}_n drawn from an arbitrary origin; $\mathbf{K} = 2\pi(\mathbf{s} - \mathbf{s}_0)/\lambda$, where λ is the X-ray wavelength and \mathbf{s} and \mathbf{s}_0 are unit vectors parallel respectively to the scattered and incident X-ray beams. The sums each extend over the N atoms in the irradiated sample.

We consider the scattering from an alloy single crystal whose atoms are equal in size; the mean atomic positions then lie on sites of a periodic lattice. Let \mathbf{u}_m^T represent the instantaneous thermal displacement of an atom of type T ($T=A$ or B) from its mean position on site m , and let \mathbf{r}_{mn} represent the lattice vector from site n to site m . The local ordering of the atoms is described by $P(\mathbf{r})$, the probability that an A atom occupies a site at a distance \mathbf{r} from a site occupied by a B atom. In the limit as r increases, $P(\mathbf{r})$ approaches the value x , the atomic fraction of A atoms in the alloy.

Following the procedure outlined by Warren, Averbach & Roberts (1951), we develop equation (1) in terms of these quantities, writing for each pair of sites the set of terms corresponding to the different possible atomic arrangements, each weighted by its appropriate probability of occurrence. This can then be rearranged in the form

$$I = I_L + I_{SRO}, \quad (2)$$

where

$$I_L = \sum_m \sum_n F_m F_n^* \exp [i\mathbf{K} \cdot \mathbf{r}_{mn}] \quad (3)$$

with

$$F_m = \{x f_A \exp [i\mathbf{K} \cdot \mathbf{u}_m^A] + (1-x) f_B \exp [i\mathbf{K} \cdot \mathbf{u}_m^B]\} \quad (4)$$

and

$$I_{SRO} = x(1-x) \sum_m \sum_n \left\{ \begin{aligned} & f_A^2 \exp [i\mathbf{K} \cdot (\mathbf{u}_m^A - \mathbf{u}_n^A)] + f_B^2 \exp [i\mathbf{K} \cdot (\mathbf{u}_m^B - \mathbf{u}_n^B)] \\ & - f_A f_B [\exp [i\mathbf{K} \cdot (\mathbf{u}_m^A - \mathbf{u}_n^B)] + \exp [i\mathbf{K} \cdot (\mathbf{u}_m^B - \mathbf{u}_n^A)]] \end{aligned} \right\} \\ \times \alpha(\mathbf{r}_{mn}) \exp [i\mathbf{K} \cdot \mathbf{r}_{mn}] \quad (5)$$

with

$$\alpha(\mathbf{r}_{mn}) = 1 - (P(\mathbf{r}_{mn})/x). \quad (6)$$

The term I_L represents the fundamental crystalline reflections and the usual temperature diffuse scattering and will not be further considered here.

The term I_{SRO} represents the diffuse scattering due to local ordering of the atoms, where the nature and degree of local order are specified by the short range order parameters, $\alpha(\mathbf{r})$. The effects of temperature on this scattering are given by the complex exponentials involving the relative thermal displacements. If these thermal displacements are neglected, equation (5) reduces to the conventional expression for local order diffuse scattering introduced by Cowley (1950),

$$I_{SRO} = Nx(1-x)(f_A - f_B)^2 \sum_n \alpha(\mathbf{r}_n) \exp [i\mathbf{K} \cdot \mathbf{r}_n], \quad (7)$$

where \mathbf{r}_n is the vector from an origin atom to the

atom on site n . A review of various studies based on this equation has been given by Warren & Averbach (1953).

The purpose of the present paper is to investigate the effects of thermal vibrations on I_{SRO} . As written, equation (5) describes the diffuse scattering appropriate to a particular instant of time. In order to be able to compare with experimental data, the time dependent terms must be averaged. We shall follow initially a procedure summarized by James (1948).

We assume that the lattice vibrations are harmonic. Then it can be shown (see Ott (1935); Born & Sarginson (1941)) that

$$\langle \exp [i\mathbf{K} \cdot (\mathbf{u}_m^S - \mathbf{u}_n^T)] \rangle = \exp [-\frac{1}{2} \langle [\mathbf{K} \cdot (\mathbf{u}_m^S - \mathbf{u}_n^T)]^2 \rangle]. \quad (8)$$

Let the thermal displacements be described as a superposition of independent travelling elastic waves of the form

$$\mathbf{u}_m^S = \sum_{g,j} \mathbf{e}_{gj} a_{gj}^S \cos (\omega_{gj} t - 2\pi \mathbf{g} \cdot \mathbf{r}_m + \delta_{gj}). \quad (9)$$

Here \mathbf{e}_{gj} is a unit vector in the direction of vibration of the j th mode ($j=1, 2, 3$) of the elastic wave of wave vector \mathbf{g} ; ω_{gj} is the angular frequency of this mode; a_{gj}^S is the amplitude of vibration of an atom of type S ($S=A$ or B) in this mode; and δ_{gj} is a phase associated with this mode which, because of the continual absorption and emission of elastic waves in a crystal, may change arbitrarily many times in the course of a measurement. The sum extends over the three modes for each of the N possible wave vectors. Implicit in this formulation is the assumption that the phase of the motion of an atom due to a given mode is independent of the atom type (A or B); this is not true in an alloy with long range order, but it seems a reasonable approximation if only local order is present.

Then, using equation (9),

$$-\frac{1}{2} \langle [\mathbf{K} \cdot (\mathbf{u}_m^S - \mathbf{u}_n^T)]^2 \rangle = -\frac{1}{4} \sum_{gj} (\mathbf{K} \cdot \mathbf{e}_{gj})^2 \\ \times \{ \overline{(a_{gj}^S)^2} + \overline{(a_{gj}^T)^2} - 2 \overline{(a_{gj}^S a_{gj}^T)} \cos (2\pi \mathbf{g} \cdot \mathbf{r}_{mn}) \}. \quad (10)$$

But

$$\frac{1}{2} \sum_{gj} (\mathbf{K} \cdot \mathbf{e}_{gj})^2 \overline{(a_{gj}^S)^2} = 2M_S, \quad (11)$$

where $2M_S$ is the exponent of the customary Debye-Waller factor for atoms of type S in this lattice. Thus

$$-\frac{1}{2} \langle [\mathbf{K} \cdot (\mathbf{u}_m^S - \mathbf{u}_n^T)]^2 \rangle = -(M_S + M_T) + D_{ST}(\mathbf{r}_{mn}), \quad (12)$$

where we have defined

$$D_{ST}(\mathbf{r}_{mn}) = \frac{1}{2} \sum_{gj} (\mathbf{K} \cdot \mathbf{e}_{gj})^2 \overline{(a_{gj}^S a_{gj}^T)} \cos (2\pi \mathbf{g} \cdot \mathbf{r}_{mn}). \quad (13)$$

In evaluating $D_{ST}(\mathbf{r}_{mn})$ several approximations are adopted concerning the lattice vibrations.

We assume that the amplitude of vibration in any given mode is the same for both types of atoms, i.e., $a_{gj}^A = a_{gj}^B = a_{gj}$. Then $M_A = M_B = M$ and $D_{ST}(\mathbf{r}_{mn}) = D(\mathbf{r}_{mn})$, also independent of atom type.

We assume that the temperature is sufficiently high so that there is equipartition of energy among the various modes of vibration. By comparing the average lattice energy written in terms of atomic kinetic energies with that given in terms of the mean energy per mode, kT , one finds that $\bar{a}_{gj}^2 = 2kT/Nm\omega_{gj}^2$, where m is the mean atomic mass, k is the Boltzmann constant and T , the absolute temperature. Then

$$D(\mathbf{r}_{mn}) = (kT/Nm) \sum_{gj} (\mathbf{K} \cdot \mathbf{e}_{gj} / \omega_{gj})^2 \cos(2\pi \mathbf{g} \cdot \mathbf{r}_{mn}). \quad (14)$$

We assume that the crystal is elastically isotropic. Then

$$\sum_j \frac{(\mathbf{K} \cdot \mathbf{e}_{gj})^2}{\omega_{gj}^2} = \frac{|\mathbf{K}|^2}{4\pi^2 g^2} \left\{ \frac{1}{\langle V_g \rangle^2} + \left(\frac{1}{V_{gt}^2} - \frac{1}{V_{gl}^2} \right) \left(\frac{1}{3} - \cos^2 \alpha \right) \right\}. \quad (15)$$

where α is the angle between \mathbf{K} and \mathbf{g} . $\langle V_g \rangle$, an average phase velocity for modes of wave vector \mathbf{g} , is defined in terms of the corresponding longitudinal and transverse mode phase velocities, V_{gl} and V_{gt} , by the relation

$$1/\langle V_g \rangle^2 = \frac{1}{3} \left\{ (1/V_{gl}^2) + (2/V_{gt}^2) \right\}. \quad (16)$$

We now approximate the actual first Brillouin zone by a sphere of the same volume, v ; the radius of this sphere is g_m . Since the density of wave vectors in the Brillouin zone is N/v , a very large number, the summation over wave vectors in equation (14) is well approximated by an integration. Writing this in terms of polar coordinates oriented along \mathbf{r}_{mn} , the angular integration can be carried out, giving

$$D(\mathbf{r}_{mn}) = \left\{ \frac{kT|\mathbf{K}|^2}{\pi m v} \int_0^{g_m} \frac{1}{\langle V_g \rangle^2} dg \right\} \times \left\{ [1 - \gamma(r_{mn})] + (\cos^2 \mu - \frac{1}{3}) \sigma(r_{mn}) \right\}, \quad (17)$$

where μ is the angle between \mathbf{K} and \mathbf{r}_{mn} , and where $\gamma(r)$ and $\sigma(r)$ are defined by the relations

$$[1 - \gamma(r)] \int_0^{g_m} \frac{1}{\langle V_g \rangle^2} dg = \int_0^{g_m} \frac{1}{\langle V_g \rangle^2} \frac{\sin 2\pi r g}{2\pi r g} dg \quad (18)$$

and

$$[\sigma(r)] \int_0^{g_m} \frac{1}{\langle V_g \rangle^2} dg = \int_0^{g_m} \left(\frac{1}{V_{gt}^2} - \frac{1}{V_{gl}^2} \right) \times \left\{ 3 \frac{\sin 2\pi r g - 2\pi r g \cos 2\pi r g}{(2\pi r g)^3} - \frac{\sin 2\pi r g}{2\pi r g} \right\} dg. \quad (19)$$

The customary Debye-Waller exponent $2M$, defined by equation (11), can be evaluated by making exactly the same approximations, giving

$$2M = \left\{ \frac{kT|\mathbf{K}|^2}{\pi m v} \int_0^{g_m} \frac{1}{\langle V_g \rangle^2} dg \right\}. \quad (20)$$

Thus we can write

$$D(\mathbf{r}_{mn}) = 2M \left\{ [1 - \gamma(r_{mn})] + (\cos^2 \mu - \frac{1}{3}) \sigma(r_{mn}) \right\} \quad (21)$$

$$= 2M \{ 1 - \varphi(\mathbf{r}_{mn}) \}. \quad (22)$$

The analytic forms for $D(\mathbf{r}_{mn})$, equation (17), and $2M$, equation (20), appear to depend in a very similar manner on the approximations of equipartition of energy, elastic isotropy, and a spherical Brillouin zone. Now the factor $2M$ can be determined experimentally. Thus if $D(\mathbf{r}_{mn})$ is evaluated from equations (21) or (22), using an experimental value for $2M$, it seems reasonable to expect that the resulting expression will be essentially independent of the limitations of these approximations.

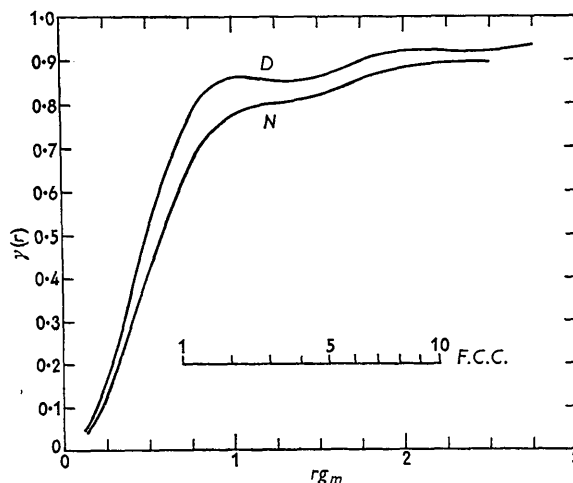


Fig. 1. Calculated curves of $\gamma(r)$ for two models of the dispersion of elastic waves. Curve N is obtained on assuming that there is no dispersion; curve D is obtained on assuming that the dispersion is the same as that for a simple linear chain. The inset scale indicates the abscissa values for the first ten neighbors in a f.c.c. lattice.

The functions $\gamma(r)$ and $\sigma(r)$ depend on the dispersion of the elastic waves. Numerical calculations have been made for two widely different models—model N , which assumes no dispersion, i.e., velocities independent of wavelength; and model D , which assumes the dispersion in a given branch to be that for a linear chain with only nearest neighbor interactions, i.e.,

$$V_g = V_0 \sin \frac{\pi g}{2 g_m} / \frac{\pi g}{2 g_m}. \quad (23)$$

Values of $\gamma(r)$, the major term, are plotted in Fig. 1 for both models as a function of the product rg_m ; the inserted scale indicates the values of rg_m for the first ten neighbors in a monatomic face-centered cubic lattice. Despite the considerable difference between the two models, the values of $\gamma(r)$ for the two cases are quite similar, differing by only 15% for nearest neighbors and by less than 10% for all other neighbors. This same insensitivity to the dispersion relations is also found for the function $\sigma(r)$. The calculation based on model D , physically the more realistic, should thus serve as a reasonable approximation for real crystals. Values for this case are listed in Table 1.

Table 1. Calculated parameters for linear chain dispersion

rg_m	$\gamma(r)$	$A^*\sigma(r)$	rg_m	$\gamma(r)$	$A^*\sigma(r)$
0.000	0.0000	0.0000	1.125	0.8605	0.0977
0.125	0.0428	0.0166	1.250	0.8527	0.0644
0.250	0.1587	0.0613	1.500	0.8607	0.0450
0.375	0.3228	0.1181	1.750	0.8982	0.0588
0.500	0.5000	0.1708	2.000	0.9208	0.0573
0.625	0.6562	0.2011	2.250	0.9193	0.0386
0.750	0.7710	0.2038	2.500	0.9208	0.0298
0.875	0.8367	0.1801	2.750	0.9348	—
1.000	0.8607	0.1394			

* $A = \frac{1}{\langle V_0 \rangle^2} / \left(\frac{1}{V_{0l}^2} - \frac{1}{V_{0t}^2} \right)$, whose value depends on the elastic constants of the crystal being studied. If $V_{0l} = 2V_{0t}$, then A equals unity.

From equations (18), (12) and (22) we now have

$$\langle \exp [i\mathbf{K} \cdot (\mathbf{u}_m^s - \mathbf{u}_n^t)] \rangle = \exp [-2M\varphi(\mathbf{r}_{mn})]. \quad (24)$$

Neglecting surface effects, the double sum of equation (5) is replaced by N times a single sum over all sites, and the average intensity is given finally as

$$\bar{I}_{SRO} = Nx(1-x)(f_A - f_B)^2 \sum_n \alpha(\mathbf{r}_n) \times \exp [-2M\varphi(\mathbf{r}_n)] \exp [i\mathbf{K} \cdot \mathbf{r}_n], \quad (25)$$

where \mathbf{r}_n is the lattice vector from the site of the origin atom to site n .

The presence of thermal vibrations thus effectively causes each short range order coefficient to be modified by an appropriate exponential damping factor. These damping factors depend on temperature and on scattering angle, as is shown by the relation (see, for example, James (1948))

$$2M = 12h^2T / (mk\Theta^2) \{ \Phi(x) + \frac{1}{4}x \} \sin^2 \theta / \lambda^2, \quad (26)$$

where h , Θ and 2θ are respectively Planck's constant, the X-ray Debye temperature, and the scattering angle. The bracketed function, $\{ \Phi(x) + x/4 \}$, where $x = \Theta/T$, is approximately unity for $T \geq \Theta$. There is also a dependence on interatomic separation, given by $\varphi(\mathbf{r})$; this arises from the fact that atoms close together on a lattice vibrate more nearly in phase on the average than do atoms that are widely separated and thus have a smaller mean square relative displacement.

It is often convenient to describe the diffuse scattering in terms of reciprocal space coordinates. For the cubic lattices under consideration we can write

$$\mathbf{r}_n = \frac{1}{2}(l\mathbf{a}_1 + m\mathbf{a}_2 + n\mathbf{a}_3), \quad (27)$$

where the \mathbf{a}_i are the usual cubic axes and where l , m , and n are integers. For face-centered cubic lattices, $l+m+n$ must be an even number, and for body-centered cubic lattices l , m , and n must be either all odd or all even. The diffraction vector can be written

$$\mathbf{K} = 2\pi(h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3), \quad (28)$$

where the \mathbf{b}_i are the usual reciprocal cell axes and where h_1 , h_2 , and h_3 are continuous variables whose integral values correspond to the Miller indices for possible crystalline reflections. Then, taking account of the center of symmetry of these lattices, equation (25) becomes

$$\frac{\bar{I}_{SRO}}{Nx(1-x)(f_A - f_B)^2} = \sum_l \sum_m \sum_n \alpha_{lmn} \times \exp [-2M\varphi_{lmn}] \cos \pi(lh_1 + mh_2 + nh_3). \quad (29)$$

For powder patterns the equation for the diffuse scattering is obtained by averaging the terms in equation (25) as \mathbf{r}_n takes with equal probability all orientations with respect to \mathbf{K} . The result can be expressed as a power series in the quantity $2M\sigma_i$, of which the first terms are

$$\frac{\bar{I}_{SRO}}{Nx(1-x)(f_A - f_B)^2} = \sum_i C_i \alpha_i \times \exp [-2M\gamma_i] \left\{ \frac{\sin Kr_i}{Kr_i} - 2M\sigma_i F_1(Kr_i) + \dots \right\}, \quad (30)$$

where

$$F_1(Kr) = \frac{2}{3} \left\{ 3 \frac{\sin Kr - Kr \cos Kr}{(Kr)^3} - \frac{\sin Kr}{Kr} \right\}. \quad (31)$$

The summation extends over the various shells of neighboring atoms; C_i is the number of neighbors in the i th shell, and $K = |\mathbf{K}| = (4\pi \sin \theta) / \lambda$. Values of the quantity $\sigma F_1(Kr)$ are always small; for example, for aluminum the maximum value is approximately 0.04.

Predicted effects

To illustrate the temperature effects predicted, a calculation has been made of the short range order diffuse scattering from a face-centered cubic single crystal, first neglecting and then including the exponential

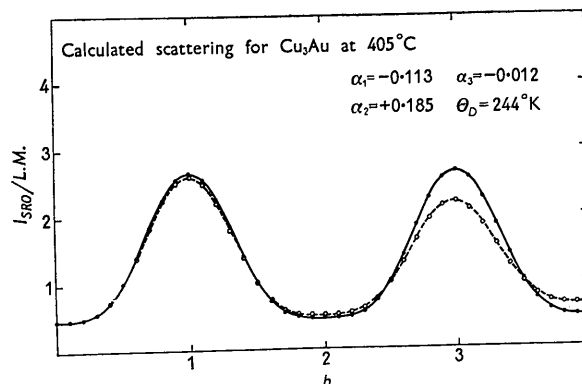


Fig. 2. Calculated curves of short range order scattering without (solid lines; equation (7)) and with (dashed lines; equation (25)) inclusion of the exponential temperature factors. The intensities, in units of the Laue monotonic scattering, are given as a function of position along a [100] axis in reciprocal space for a model corresponding to Cu_3Au at 405 °C.

damping factors of equation (29). The parameters used correspond approximately to those of the alloy Cu_3Au at 405°C . ($\sim 15^\circ$ above T_c). The calculated intensities, in units of the Laue monotonic scattering, $Nx(1-x)(f_A - f_B)^2$, are shown in Fig. 2 as a function of position along the [100] axis in reciprocal space.

The scattering curve calculated from the temperature-independent theory is periodic in reciprocal space. The scattering curve calculated from the theory including the exponential temperature factors is not periodic. Instead the modulations in the scattering, the diffuse peaks and minima, show an attenuation which increases rapidly with increasing scattering angle. In this example the intensity of the lowest angle diffuse peak, at $h=1$, is reduced by 2.3%, while the intensity of the second diffuse peak, at $h \simeq 3$, is reduced by 17.7%. The magnitude of the attenuation increases also with increasing temperature. A secondary effect of the temperature factors is to shift the maxima of the diffuse peaks to smaller angles. The displacement is small; in this example the second diffuse peak occurs at $h=2.98$ rather than $h=3$.

The monotonic background scattering characteristic of a completely random alloy, the term for $l=m=n=0$ in equation (29), is not affected by a temperature factor. There can be no thermal displacement of an atom relative to itself, so $\varphi(0)=0$. In contrast, Münster & Sagel (1957) have predicted a large attenuation of this monotonic scattering. Their result appears to have been caused by the adoption of a poor mathematical approximation.

Experimental evidence

Several examples of short range order diffuse scattering have been reported that show an attenuation of the intensity of the diffuse peaks with increasing $(\sin \theta)/\lambda$ of the type predicted. Muldrew (1954), studying Au-doped β -AgZn, found the (300) diffuse peak to be weaker than the (100) diffuse peak. Keating & Walker (1959), in a neutron diffraction study of β -CuZn, found the (111) diffuse peak to be weaker than the (100) diffuse peak. Borie (1957) reported a related effect for quenched Cu_3Au ; the Fourier coefficients for the (300) diffuse peak were smaller than the corresponding coefficients for the (100) diffuse peak, the ratios approaching the value $\exp[-(2M+2M')]$. (The artificial temperature factor $2M'$ arises from long range elastic strains due to differing atomic size.)

The temperature dependence can be investigated by measuring the scattering from a quenched alloy at 300°K . and at 78°K ., temperatures at which no change in the local order should be expected. Such measurements have been made on a single crystal of nominal composition Cu_2Au cut with faces parallel to (100) planes and quenched from 450°C . Crystal monochromated Mo $K\alpha$ radiation was used, with the X-ray tube operated at 30 kV. peak to avoid the presence of half-wavelength radiation, and the diffuse

scattering was measured along the [100] axis in reciprocal space from the (200) reflection to the (10,00) reflection. The measured intensities, corrected only for fluorescence and cosmic ray background, are plotted in Fig. 3. The off-scale peaks at $h=2, 4, 6$, etc., are the fundamental crystalline reflections (200), (400), (600), etc. and their associated temperature diffuse scattering. The diffuse peaks at $h \simeq 3, 5, 7$, and 9 are due to short range order. The asymmetry of the background on either side of the short range order peaks results from appreciable atomic size effects (see Warren, Averbach & Roberts (1951)). Both curves show the strong decrease of intensities with increasing $(\sin \theta)/\lambda$ that is characteristic of the angular dependence of the atomic scattering factors.

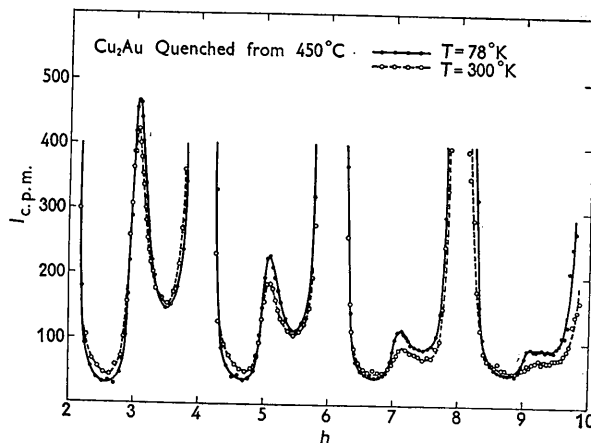


Fig. 3. Experimental measurements of the scattering along the [100] axis in reciprocal space from a quenched single crystal of the alloy Cu_2Au at sample temperatures of 78°K . and 300°K . Crystal-monochromated Mo $K\alpha$ was used, and the measured intensities have been corrected only for fluorescence and cosmic ray background.

Comparison of the short range order diffuse scattering peaks at the two temperatures clearly shows the predicted temperature effects. The peak intensities at 300°K . are lower than the corresponding intensities at 78°K ., and the amount of this thermal attenuation increases rapidly with increasing distance out in reciprocal space. An accurate quantitative check of the theory is not possible from these measurements, since the short range order scattering is accompanied both by a varying, unknown amount of temperature diffuse scattering and by strong atomic size effects. Within the rather large limits of error caused by these factors, which, for example, corresponds to an uncertainty of approximately $\pm 30\%$ of the observed attenuation for the peak at $h=7$, the observed attenuations associated with this change in temperature are in agreement with the theoretical predictions.

Discussion and conclusions

An approximate theory of local order diffuse scattering

from binary alloys has been developed in which the effects of the thermal vibrations are explicitly described. Briefly, the thermal effects appear as appropriate exponential temperature factors modifying the various short range order coefficients in the usual Fourier series representation of the diffuse scattering. These temperature factors attenuate the modulations in the diffuse scattering (the peaks and minima), with the amount of attenuation increasing rapidly with increasing scattering angle and temperature. The Laue monotonic scattering term is not affected.

In the derivation of this theory a number of approximations have been adopted concerning the nature of the lattice vibrations. Fortunately, most of these approximations seem to have little effect on the final expression, since the relevant factor in the final form can be expressed as the product of two terms, one relatively insensitive to the various approximations and the other an experimentally measurable quantity.

One approximation should be examined further. It has been assumed that the amplitude of vibration in any given mode is the same for both types of atoms. There is no information known about the vibrations of atoms in a binary alloy with only local order, so the reliability of this approximation is uncertain, but intuitively it seems to be the most restrictive step in the theory. The dependence of the final expression on this approximation can be investigated by adopting instead a less restrictive approximation, namely, that the ratio of the amplitudes of vibration in any given mode for the two types of atoms be a constant, i.e., $\alpha_{g_j}^B/\alpha_{g_j}^A = C$. Then $M_B = C^2 M_A$. If we proceed as before, assuming in addition that the quantity

$$(M_A + M_B - 2\sqrt{M_A M_B})$$

is negligible compared to unity, we obtain finally

$$\begin{aligned} \bar{I}_{SRO} = Nx(1-x) \sum_n \{f_A \exp[-M_A \varphi(\mathbf{r}_n)] - f_B \\ \times \exp[-M_B \varphi(\mathbf{r}_n)]\}^2 \alpha(\mathbf{r}_n) \exp[i\mathbf{K} \cdot \mathbf{r}_n]. \end{aligned} \quad (32)$$

The temperature effects predicted by this equation are qualitatively the same as those predicted by equation (25), but there can be significant quantitative differences if M_A and M_B differ widely. Since marked differences between M_A and M_B do exist for some alloys with long range order, one should expect that similar differences between Debye-Waller factors may also exist for certain alloy systems with only local order. We must conclude then that in some cases, for which at present there are no dependable criteria for identification, equation (25) may serve only as a first approximation.

The general features of the predicted temperature effects have been confirmed by experimental observations. Results for several alloys have shown an attenuation of the short range order diffuse scattering peaks that increased with increasing $(\sin \theta)/\lambda$. Measurements on the alloy Cu_2Au given here show that this

attenuation increases both with increasing $(\sin \theta)/\lambda$ and with increasing temperature, and the agreement between the theoretical predictions and the measured temperature dependence of the attenuation gives a semi-quantitative confirmation of the theory. A more accurate quantitative comparison of the theory with experimental data is still to be desired.

The magnitudes of these thermal effects are not negligible, particularly in the normal high-angle region in which most short range order diffuse scattering studies have been made. This is illustrated both by the calculated scattering curves of Fig. 2, where the model approximates Cu_3Au at 405 °C., and by the experimental scattering curves of Fig. 3. Such attenuated scattering curves, if analyzed by the usual Fourier transform procedure, will give 'experimental' values for the short range order parameters that are too small in magnitude as compared with the true values. As an example, Fourier transforms have been made of the temperature-affected diffuse scattering curve of Fig. 2 from $h=2$ to $h=4$, where conditions correspond quite closely to those in the study by Cowley (1950), and the resulting coefficients interpreted by means of the customary temperature-independent theory, equation (7), to give 'experimental' values for the short range order parameters. The value obtained for the first neighbor parameter, α_1 , is -0.085 , 24% smaller in magnitude than the true value of -0.113 , and the values for the higher neighbor parameters are attenuated by an even greater percentage. Thus in these conditions the thermal effect is quite important. At the smaller angles the effect is of course much less; a similar analysis of this scattering curve from $h=0$ to $h=2$ gives values for the short range order parameters that are attenuated by only approximately 3%.

The neglect of this temperature effect appears to be a significant source of error in past experimental studies of short range order in alloys. The majority of the single crystal studies (Cowley (1950), Sutcliffe & Jaumot (1953), Roberts (1954), Batterman (1957)) were made at such temperatures and scattering angles as would lead to thermal attenuations comparable to that for our model of Cu_3Au in the neighborhood of $h=3$. The short range order parameters reported for these alloys thus can all be estimated to be roughly 20% too small in magnitude as a result of this effect. In the single crystal studies made at lower temperatures or smaller scattering angles (Norman & Warren (1951), Suoninen & Warren (1958)) the errors due to this effect are of course much less. The errors in the short range order parameters determined from powder pattern diffuse scattering measurements are more difficult to estimate, since the temperature factors enter the analysis in a rather complicated manner (Flinn, Averbach & Rudman (1954)). As in the single crystal cases, thermal attenuation has caused the measured parameters to be too small.

The value of using low-angle diffuse scattering

measurements for studies of local order in alloys is again emphasized. In the low-angle region the Compton scattering, the thermal diffuse scattering, atomic size effects and thermal attenuations are all at their smallest, so that with low-angle measurements one can obtain the greatest possible accuracy of interpretation.

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Ultrasonic Methods of Determining Elasto-Optic Constants of Uniaxial and Biaxial Crystals*

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Ultrasonic methods of studying the photoelastic behaviour of crystals, suggested by Mueller in 1938, have heretofore been applied only to glasses and cubic crystals. The method has been applied to uniaxial and biaxial crystals. Both theory and experiment are given. The ultrasonic methods replace the more difficult and less accurate interferometric methods for determining the elasto-optic constants. Results obtained on calcite, quartz, and barite are presented.

Introduction

Studies on the photoelastic behavior of solids have as their aim the determination of elasto-optic and piezo-optic constants (the p 's and q 's of Pockels (1906)) for the given solid. In an actual experiment, one determines the small changes in refractive index in different directions when a stress of known magnitude is applied in certain convenient directions. The bulk of the results obtained for p 's and q 's is based on the optical measurements in which one obtains relative path retardations using any one of the well known interferometers. The discovery of ultrasonics and the effect of a sound field on a transparent crystal through which polarized light is passing, led Bergmann & Fues (1936) to indicate the possibility of studying the photo-elastic constants of

glasses by observing the polarized diffraction spectra from a point source. The situation very much improved when Hiedemann & Hoesch (1936) showed how easily line diffraction patterns could be obtained. The theory of diffraction of light in solids given by Nath & Mueller (1938) was experimentally verified by Hiedemann (1938). Subsequently, Mueller (1938) suggested in detail various methods of obtaining the elasto-optic constants of glasses and cubic crystals by studying the polarized diffraction spectra. Using the procedure suggested by Burstein *et al.* (1948), Vedam (1950) and Iyengar (1953) obtained all the photo-elastic constants of some glasses and cubic crystals by combining the relative path retardation methods using the Babinet compensator with the ultrasonic method due to Mueller (1938). It may be pointed out that the ultrasonic methods yield results to the same order of accuracy as the Babinet compensator method, whereas the interferometric methods often yield results differ-

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