Acta Cryst. (1977). A**33**, 342–343

An unusual small-particle-size effect.

By C. B. Walker, *Army Materials and Mechanics Research Center, Watertown, Massachusetts* 02172, *USA*

(*Received* 30 *September* 1976; *accepted* 20 *November* 1976)

A calculation shows that a small particle size can cause extra broadening and increased integrated intensities for reflections with rapidly varying geometrical structure factors.

The diffraction effect usually anticipated for a small crystallite particle size is a broadening of the intensity distribution at each reciprocal-lattice point, the same for all reflections, whose shape depends on the external form of the crystal. James (1948) has remarked that if the crystallite size is very small, the intensity distribution around a reciprocal-lattice point may show additional appreciable modifications as a result of the variation of the structure factor through the region of the broadened interference function. This note presents a calculation demonstrating one kind and size of modification that may occur for real physical systems.

We consider an ω-phase particle that is a coherent precipitate in a b.c.c. matrix, as is found in several Zr and Ti-base alloys. The ω-phase lattice is hexagonal, with $\mathbf{c}\parallel[111]_{\text{b.c.c.}}$ and $\mathbf{a}_1\parallel[\bar{1}\bar{1}2]_{\text{b.c.c.}}$ and with atoms at 0,0,0 and $\pm(\frac{1}{3},\frac{2}{3},\frac{1}{3}+\frac{1}{6}\delta)$, where δ varies between 0 (untransformed b.c.c.) and 1 (the final AlB_2 structure) depending on composition, thermal history, *etc*. The geometrical structure factor for reflections not coincident with matrix reflections can be written

$$F/f=4\sin\frac{\pi}{3}[h_1-h_2+(1-\tfrac{1}{2}\delta)h_3]\sin\frac{\pi}{6}\delta h_3$$

where h_1, h_2, and h_3 are reciprocal-space variables whose integral values are the reflection Miller indices; its maximum rate of change in a plane, $h_3=$constant, is along the $[1\bar{1}.0]$ direction. Our particle, approximately an average particle in an alloy of Ti with 19% V quenched from 1000°C, has the form of a short rod, with a length of $24|\mathbf{c}|=67$ Å and an 80-unit-cell cross-section, shown in the inset of Fig. 1, with an average diameter of $9{\cdot}4|\mathbf{a}|=43$ Å, and its structural parameter δ is 0·829. The particle interference function gives disc-like regions of slightly elliptical cross-section, with the disc axis parallel to [00.1] and with a thickness:average diameter ratio at half-maximum of 0·55.

We look first at the (10.3) reflection. The dashed curve in Fig. 1 gives the intensity – $(F/f)^2$ times the normalized interference function – as a function of distance from the reciprocal-lattice point in the $[1\bar{1}.0]$ direction, *if F/f is constant*, equal to its value at the reciprocal-lattice point. The dotted curve shows the actual variation of $(F/f)^2$ along this line, and the solid curve shows the modified intensity distribution along this line that is obtained using the actual values of $(F/f)^2$ in the calculation. The structure factor variation here causes a peak displacement of $-0{\cdot}020(\mathbf{a}_1^*-\mathbf{a}_2^*)$, a peak intensity increase of 18%, and an integrated intensity increase of 6·6%. A similar calculation for the weaker 10.2 reflection shows a peak displacement of $+0{\cdot}026(\mathbf{a}_1^*-\mathbf{a}_2^*)$, a peak intensity increase of 35%, and an integrated intensity increase of 14%, while the effects for other reflections (10.1, 00.1, 00.2, and $\bar{1}$0.3) with intensities comparable to or greater than the 10.3 are an order of magnitude smaller.

In order to make a comparison with real physical systems we extend the calculation to include a number of such particles distributed throughout the matrix with a common c-axis orientation but with $\mathbf{a}_1$ axes oriented randomly among the three equivalent $[\bar{1}\bar{1}2]$ directions. Since these particles are separated by varying steps of $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{c}$, we assume that interparticle interferences can be neglected and calculate the total intensity as an average over the intensities for the three orientations of $\mathbf{a}_1$. This averaging eliminates the peak displacements but adds corresponding extra broadening. The net effects of the structure factor variation on reflections from our system of particles are: the 10.1, 00.1, 00.2, and $\bar{1}$0.3 reflections show changes of less than 0·5% both in integrated intensity and in the average breadth (FWHM) perpendicular to $\mathbf{c}^*$, the 10.3 reflection shows a 4·9% increase in breadth and a 6·6% increase in integrated intensity, the $\bar{1}$0.2 reflection shows a 10% increase in breadth and a 14% increase in integrated intensity, and those reflections with increased breadths show cross-sections with increased departures from circular symmetry.

The large effects here result from the presence of a rapidly varying geometrical structure factor and so must depend significantly on the value of the parameter δ. The size of these effects appears to vary approximately inversely with the particle cross-sectional area, *e.g.* calculations for a system of similar particles with a 30-unit-cell cross-section show increases of 26% in breadth and 35% in integrated intensity for

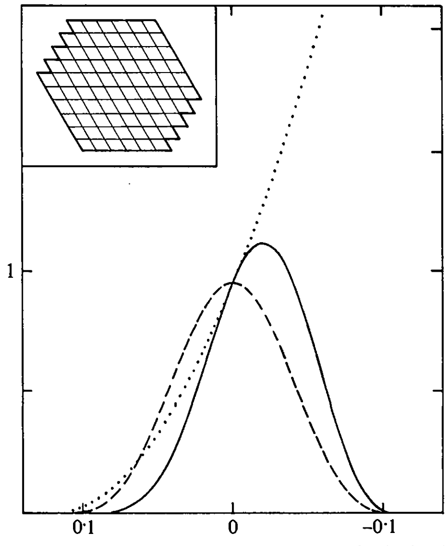

Fig. 1. Intensity functions *vs* distance (in units of $|\mathbf{a}^*|$) in the $[1\bar{1}.0]$ direction from the 10.3 reciprocal-lattice point. The dashed curve gives the intensity calculated with $(F/f)^2$ assumed to be constant, the dotted curve gives the actual variation of $(F/f)^2$, and the solid curve gives the intensity obtained from the actual $(F/f)^2$ values. The inset shows the 80-unit-cell cross-section of the model ω-particle.

$\bar{1}0.2$ and increases of 13% in breadth and 17% in integrated intensity for 10.3, while the four insensitive reflections show changes of less than 1·3%. Real alloys have shown ω-particles with average sizes as small as a $7|\mathbf{c}|$ length and only a 4-unit-cell cross-section (Keating & LaPlaca, 1974).

We have presented here a calculation of a small-particle-size effect for a model of ω-phase precipitates in alloys that results in increases in breadths and integrated intensities for certain sensitive reflections. The important feature of the model is the existence of reflections with rapidly varying geometrical structure factors, so similar effects should be expected for sensitive reflections of other multi-atom structures of sufficiently small particle size. These calculations are given some support by our observation (Walker, unpublished) of excess broadening of sensitive ω-phase reflections from a quenched alloy of Ti with 19% V, but no quantitative comparison has yet been possible.

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Acta Cryst. (1977). A**33**, 343

X-ray linear absorption coefficient of silicon for Cu *Kα* and Mo *Kα* radiations.

By J. L. Lawrence. *School of Physical Sciences, The University, St Andrews, Fife, Scotland*

(*Received* 26 *May* 1976; *accepted* 24 *August* 1976)

The X-ray mass attenuation coefficients of silicon for Cu $K\alpha$ radiation have been measured and found to be 56·9 (3) and 6·09 (3) cm^2 g^{-1} respectively.

A method of determining accurate X-ray attenuation coefficients using single crystals has been described by Lawrence & Mathieson (1976). The method involves measuring the intensity of the transmitted beam, I_t, passing through a specimen of thickness t, whose faces are accurately parallel and whose cross section is greater than that of the main beam, as the beam makes varying angles φ with the normal to the crystal face. Then,

$$I_t = I_0 \exp(-\mu t/\cos\varphi) = I_0 \exp(-n\mu t).$$

A plot of $\log_e I_t$ against n will yield values of μt from which μ can be determined. The value of I_0 can also be obtained and compared with the directly measured value. The presence of white radiation and harmonic components in the main beam may make these values different and may also lead to deviations from linearity in the plot.

This possible source of error has been eliminated by monochromatizing the main beam with the 111 reflexion from a near-perfect silicon crystal. Since the 222 reflexion is very weak, no harmonics should be present and the very small divergence of the diffracted beam will eliminate variations in the path length through the crystal which may be significant for large n.

No recent experimental determination of the absorption coefficient of silicon appears to have been carried out and because of its large abundance and of its large number of chemical compounds, it was felt that an accurate measurement of its absorption coefficient would be useful.

A single crystal of silicon, whose cross section was a square of side 0·7 cm, was used. The thickness of the crystal was measured systematically over the surface traversed by the X-ray beam with a linear differential transducer (model ER/0·100, manufactured by Sangamo Weston Controls Limited) which had been carefully calibrated using slip gauges. The mean thickness was found to be 0·05107 (15) cm.

With Cu $K\alpha$ radiation, the beam from the monochromator was collimated by a circular aperture of radius 0·1 mm and the crystal centred on a two-circle spectrometer. The intensities were measured by a scintillation counter attached to a Siemens counting chain. For each value of φ, four equivalent transmitted intensities were measured, *i.e.* at $\pm\varphi$ and $180\pm\varphi$, and the average intensity used. Intensities were measured at intervals of 5° from $\varphi=0$ to $\varphi=30°$ and at intervals of 2° from $\varphi=32$ to $\varphi=60°$.

The count rate at $\varphi=0°$ was set to about 4000 counts per second. Sufficient counts were recorded at each setting to ensure that the counting statistics error on the average of the four settings was of the order of 1%. The errors quoted are those obtained from a least-squares fit.

From the resulting graph of $\log_e I_t$ against n, a value of μt of 6·76 (3) was obtained giving $\mu = 132·4$ (7) cm^{-1} and $\mu/\varrho = 56·9$ (3) cm^2 g^{-1} taking $\varrho = 2·3283$ g cm^{-3} (Straumanis & Aka, 1952). The value quoted in *International Tables for X-ray Crystallography* (1974) is 65·32 cm^2 g^{-1} with an error in the range 2 to 5%. Even if the maximum error is assumed, it must be concluded that the two values are significantly different.

With Mo $K\alpha$ radiation, the values were $\mu = 14·18$ (7) cm^{-1} and $\mu/\varrho = 6·09$ (3) cm^2 g^{-1}. This can be compared with the value of 6·533 cm^2 g^{-1} quoted in *International Tables* (1974).

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