FIGGIS, B. N., GERLOCH, M. & MASON, R. (1969) *Proc. Roy. Soc.* A**309**, 91.
FISCHER, H. & PÜTZER, B. (1926). *Hoppe Seyler Z. Physiol. Chem.* **154**, 39.
FISCHER, H., TREIBS, A. & ZEILE, K. (1930). *Hoppe Seyler Z. Physiol. Chem.*. **193**, 1.
GOLDANSKII, V. I. & HERBER, R. H. (1968). *Chemical Applications of Mössbauer Spectroscopy*. New York: Academic Press.
HEBERLE, J. & FRANCO, S. (1968*a*). *Z. Naturforsch.* **23a**, 1439.
HEBERLE, J. & FRANCO, S. (1968*b*). *Bull. Amer. Phys. Soc.* **13**, 60.
JOHNSON, D. P. & DASH, J. G. (1968). *Phys. Rev.* **172**, 983.
KENDREW, J. C. & PARRISH, A. G. (1956). *Proc. Roy. Soc.* A**238**, 305.
KOENIG, D. F. (1965). *Acta Cryst.* **18**, 663.
MÖSSBAUER, R. L. & SHARP, D. H. (1964). *Rev. Mod. Phys.* **36**, 410.
MUIR, A. H., ANDOR, H. I. & COOGAN, H. M. (1966). *Mössbauer-Effect Data Index*, 1958-1965. New York: John Wiley.
NUSSBAUM, R. H., HOWARD, D. G., NEES, W. L. & STEEN, C. F. (1968). *Phys. Rev.* **173**, 653.
TEALE, F. W. J. (1959). *Biochim. Biophys. Acta*, **35**, 543.
THEORELL, A. H. & AKESON, A. (1950). *Ann. Sci. Fenn.* Ser. A II **60**, 303.
TRAMMELL, G. T. (1962). *Phys .Rev.* **126**, 1045.
WATSON, H. C. (1970). Department of Biochemistry, Univ. of Bristol, private Mitteilung.
WEGENER, H. (1965). *Der Mössbauereffekt*, BI Hochschultaschenbuch Nr. 2/2a.

Acta Cryst. (1971). A**27**, 578

A Method for Determining Stresses in Single Crystals by X-ray Diffraction

BY S'KENG PAN* AND ROLF WEIL

Department of Metallurgy, Stevens Institute of Technology, Hoboken, New Jersey 07030, *U.S.A.*

(*Received* 21 *May* 1970 *and in revised form* 25 *March* 1971)

A method for determining the stresses in single crystals similar to that generally used for polycrystalline samples is described. The method for single crystals is more complicated because of the need for accurate alignment and consideration of anisotropic elastic constants. Means for calculating and compensating for alignment errors are included. Stress values determined by this method are compared with those determined by other independent means.

Introduction

X-ray diffraction methods are widely used to determine stresses in polycrystalline solids. However, these methods have been applied successfully to single crystals in only a few instances and then either necessitated the employment of special equipment or were limited to certain types of samples. Pseudo-Kossel patterns obtained by means of microfocus X-ray units have been used successfully by Imura (1954, 1957) and by Imura, Weissmann & Slade (1962), Ellis, Nanni, Shrier, Weissmann, Padawer & Hosokawa (1964) and Slade, Weissmann, Nakajima & Hirabayashi (1965), to determine stresses in single-crystal samples. Stresses in a special type of specimen, a vapor-deposited metal film epitaxically grown on a sodium chloride monocrystal and still attached to it were measured by Freedman (1962). Newton (1964) used conventional X-ray equipment to measure stresses in individual crystals of a large-grained piece of aluminum. But as he neglected line shifts due to errors in alignment, his results were inconsistent. No general method for determining the stresses of single crystals using conventional X-ray equipment existed prior to this study.

A procedure for determining the stresses from the shifts of X-ray diffraction lines of monocrystalline samples analogous to the widely used two-angle method was developed in connection with a study of the origins of internal stresses in electrodeposits. This method which only requires certain modifications of the generally available types of X-ray units and a special specimen holder is described here and has been named the 'two-plane method'.

The two-plane method differs from the two-angle method used for the determination of stresses in polycrystalline samples and described in almost all diffraction textbooks in two ways. The two-plane method of single crystals requires the determination of the Bragg angle from a set of planes $(h_0k_0l_0)$ nearly parallel to the surface and from a second set of planes, $(h_1k_1l_1)$ inclined at a definite angle, α.

The two-plane method differs from Bond's technique for precision lattice determination of single crystals in that the Bragg angle of the inclined plane $(h_1k_1l_1)$ must also be determined. The alignment errors for Bond's method have been considered by Burke & Tomkeieff (1968). The evaluation of the alignment errors resulting

* Presently associated with Speedway Laboratory, Union Carbide Corp. Indianapolis, Indiana 46224.

from tilting to the inclined plane is one of the contributions of this paper. The other purposes of the paper are to show how the alignment errors can be corrected and that stresses determined by the two-plane method are comparable to those obtained by other independent means.

Equations for Bragg-Angle changes due to stress and crystal alignment

The measured Bragg angles, θ^0 and θ^1 from the sets of planes, $(h_0k_0l_0)$ and $(h_1k_1l_1)$, respectively of the single-crystal specimen are related to the true angles, θ_t^0 and θ_t^1 by the equations:

$$\theta^0=\theta_t^0+\Delta\theta_\sigma^0+\Delta\theta_a^0 \quad (1)$$

$$\theta^1=\theta_t^1+\Delta\theta_\sigma^1+\Delta\theta_a^1 . \quad (2)$$

The angular shifts, $\Delta\theta_\sigma^0$ and $\Delta\theta_\sigma^1$ are related to the stresses by

$$\Delta\theta_\sigma^0=b^0\sigma_S$$
$$\Delta\theta_\sigma^1=b^1\sigma_S . \quad (3)$$

The coefficients, b^0 and b^1 are for a uniaxial state of stress, *i.e.* $\sigma_Y=\sigma_Z=0$, $\sigma_X=\sigma_S$ (the coordinates are shown in Fig. 1) and the equal biaxial case, *i.e.* $\sigma_Z=0$, $\sigma_Y=\sigma_X=\sigma_S$, respectively:

$$b^0=\frac{\nu}{E}\tan\theta^0$$
$$b^1=\frac{1}{E}[\nu-m^2(1+\nu)]\tan\theta^1 \quad (4)$$
$$b^0=\frac{2\nu}{E}\tan\theta^0$$

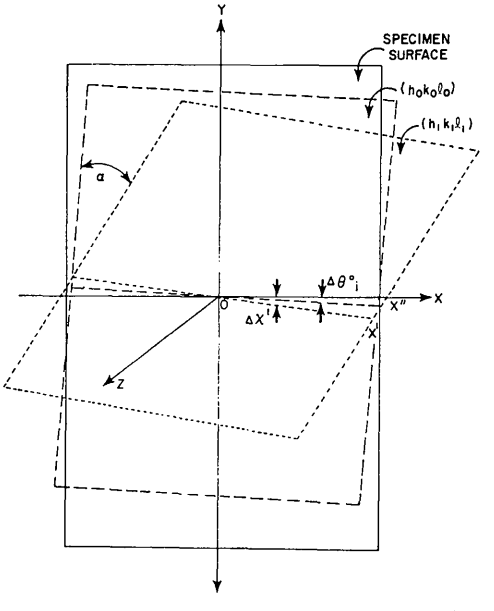

Fig. 1. Diagram showing the relationship between the plane $(h_1k_1l_1)$ and the specimen surface and $(h_0k_0l_0)$.

$$b^1=\frac{1}{E}[(1+\nu)r^2-(1-\nu)]\tan\theta^1 . \quad (5)$$

The constants, E and ν can be calculated from the elastic compliances (Greenough, 1955) by:

$$E=\{S_{11}-2[(S_{11}-S_{12})-\tfrac{1}{2}S_{44}]\,[m^2n^2+n^2r^2+m^2r^2]\}^{-1}$$
$$\nu=\frac{S_{12}+[S_{11}-S_{12})-\tfrac{1}{2}S_{44}]\,[m^2n^2+n^2r^2+m^2r^2]}{S_{11}-2[(S_{11}-S_{12})-\tfrac{1}{2}S_{44}]\,[m^2n^2+n^2r^2+m^2r^2]} \quad (6)$$

where m, n and r are the direction cosines of the normal to the diffracting plane. The definition of the compliances and values for several materials are given by Tegart (1966) and Wasilewski (1965).

The changes in the Bragg angles due to alignment are

$$\Delta\theta_a^0=\frac{(\Delta\varphi^0)^2}{(\pi/2)-\theta^0}+\Delta\theta_i^0 \quad (7)$$

$$\Delta\theta_a^1=\Delta\theta_i^0\cos\alpha+\Delta\chi^1\sin\alpha+\frac{(\Delta\varphi^0)^2-\alpha(\Delta\varphi^0)\,(\Delta\chi^1)^2}{(\pi/2)-\theta^1} . \quad (8)$$

The quantities, α, $\Delta\theta_i^0$ and $\Delta\chi^1$ are shown in Fig. 1. Equations (7) and (8) are derived in the Appendix, where $\Delta\varphi^0$ is also explained. Equations (7) and (8) are directly applicable when θ rocking curves are obtained with the counter in a fixed position. When θ–2θ scans are used, the alignment changes become

$$\Delta 2\theta_a^0=\frac{4(\Delta\varphi^0)^2}{\pi-2\theta^0}+2\Delta\theta_i^0+\frac{2\Delta Z}{R}\cos\theta^0 \quad (9)$$

$$\Delta 2\theta_a^1=2\Delta\theta_i^0\cos\alpha+2\Delta\chi^1\sin\alpha + \frac{4(\Delta\varphi^0)^2-4\alpha\Delta\varphi^0(\Delta\chi^1)}{\pi-2\theta^1}+\frac{2\Delta Z}{R}\cos\theta^1 . \quad (10)$$

where ΔZ is the distance between the specimen surface and the diffractometer axis and R is the radius of the diffractometer circle. The experimental methods for determining the various quantities in equations (7), (8), (9) and (10) are discussed in the next section.

Stress measuring procedures

The apparatus for measuring stresses in single crystals is a conventional X-ray diffractometer unit with some modifications. The apparatus used in this study is shown in Fig. 2. Molybdenum radiation was used in most tests because with short wavelength X-rays it is possible to obtain several high-order reflections in close proximity on the θ scale. Thus, for example, for a copper crystal with the [001] direction nearly parallel to the surface, the Bragg angles of the (0,0,10) {tenth order of (001)} plane and of the (339) {third order of (113)} plane occur at 78·79° and 77·42°, respectively. The X-ray tube was turned on several hours prior to making measurements in order to stabilize the beam and prevent movement of the tube due to thermal expansion. The temperature of the room was also con-

trolled within 1 °C. The X-radiation passed through a 0·1° collimator *A*. The height of the beam was restricted to 1 mm by means of slits. The X-rays impinged on the crystal *B* held in the special specimen holder.* Dials *C* and *D* determined the rotation about the *X* and *Z* axes. The θ rotation was performed by a motorized specimen-holder base* for quick scanning or manually for more accurate measurements. A scintillation counter *G* was used for its high sensitivity to Mo $K\alpha$ radiation.

The diffraction curves, *i.e.* graphs of diffracted intensity above background *vs.* the angle, θ could be obtained in two ways. The θ rocking curves were obtained by setting the counter at approximately twice the Bragg angle of the plane to be studied. The full counter window covered only with a two-mil-thick zirconium filter was able to receive radiation over a 4° range. For the θ–2θ scans, which were not extensively used because of the ΔZ error, the proper slits were mounted in front of the counter.

The actual determination of the values of the Bragg angles from the diffraction curves was performed by a step-counting method. First, while scanning usually with the motorized base, the curves were plotted on graph paper. From this chart, seven or nine points were selected. These values were spaced at equal angular intervals on both sides of the angle where the maximum intensity occurred. From the intensity *vs.* angle data three values of the Bragg angle were calculated. One value was the center of gravity of the diffraction line. The data were also fitted to the best parabolic equation as obtained by a least-squares method. The maximum-intensity point of the parabola was another value of the Bragg angle. The angle where the maximum intensity occurred was the third value. These values of the Bragg angles were substituted in the various equations.

When the θ rocking procedure was used, it was necessary that the angles be measured with the same accuracy as those on the diffractometer circle. A means of obtaining this precision while manually moving through the angle, θ is also shown in Fig. 2. One end of an arm *K* is rigidly attached to the base of the specimen holder. A small steel plate and a dial gage, *I*, are mounted on the other end of the bar. Two micrometers, *E* and *F*, are mounted on a frame, *H* which is rigidly attached to the side of the X-ray unit. In order to rotate the sample by a small angular increment, micrometer *E*, which was calibrated in 0·0001 inch was set at the desired value converted from an angular segment of arc. The arm was then moved by pushing against the metal plate with micrometer *F* until the dial gage, which was in contact with micrometer *E*, read zero again. The dial gage, which was also calibrated in units of 0·0001 inch was used so that there was always the same pressure against the micrometer. A spring *J* held the two parts of the measuring assembly together and could be easily removed for the motorized scanning.

The conversion of distances on micrometer *E* into angular units was accomplished by the use of a germanium single crystal of high perfection and aligned in the holder by the previously outlined procedure. The diffraction curves for the ninth-order reflection of the (111) plane, which was parallel to the surface, caused by Mo $K\alpha_1$ and Mo $K\alpha_2$ radiation were determined. It was possible to determine the actual value of θ which corresponded to zero on the micrometer from the known location of the $K\alpha_1$ peak. As the angle between the two peaks was also known, it could be translated into the distance between them as measured on the micrometer. The small error resulting from the fact that the micrometer measured the tangent rather than the arc was found to be negligible.

The first step in the procedure of aligning the crystal consisted of orienting the plane $(h_0k_0l_0)$ for diffraction by rotating about the *X* and *Y* axes until the reflected intensity reached a maximum. The second step was aligning the *X* direction to coincide with the zone axis of the planes $(h_0k_0l_0)$ and $(h_1k_1l_1)$. This operation was performed by a rotation about the *Z* axis and tilting about *X* by an angle equal to that between the planes again until the maximum reflected intensity was obtained. The approximate location of the zone axis had to be determined prior to this procedure from a Laue pattern.

The determination of θ^0 as defined in equation (1) involved two measurements. The zone axis had to be essentially parallel to the *X* direction during these measurements even though its location had no effect on the value of θ^0. However, the location of the zone axis affected the value of θ^1, which was also dependent on some of the factors involved in the determination of θ^0. The two measurements were the determinations of the Bragg angles, θ_0^0 and θ_π^0, which were the values of the Bragg angle measured at χ equal to zero and with the specimen rotated about the *Z* axis so that χ was equal to 180°. Then,

$$\theta^0 = \frac{\theta_0^0 + \theta_\pi^0}{2} \text{ or } \Delta\theta_i^0 = \frac{\theta_\pi^0 - \theta_0^0}{2} \qquad (11)$$

where $\Delta\theta_i^0$ is the horizontal component of the angle between the specimen surface and the plane $(h_0k_0l_0)$.

The vertical component, $\Delta\varphi^0$ of the angle between the specimen surface and the plane $(h_0k_0l_0)$, was determined similarly by measuring the Bragg angles, $\theta_{\pi/2}^0$ and $\theta_{3\pi/2}^0$, which are obtained by rotating the crystal so that χ is 90 and 270°, respectively. Then,

$$\Delta\varphi^0 = \frac{\theta_{3\pi/2}^0 - \theta_{\pi/2}^0}{2}. \qquad (12)$$

Another way of correcting the alignment error was finding the configuration so that $\Delta\varphi^0$ is zero. It can be seen from equation (7) that either positive or negative values of $\Delta\varphi^0$ result in an increase in θ^0. Therefore the minimum Bragg angle is obtained where $\Delta\varphi^0$ is zero. By determining the Bragg angle when the crystal is

* Specimen holder and motorized θ rotation made by Electronics and Alloys, Englewood, New Jersey.

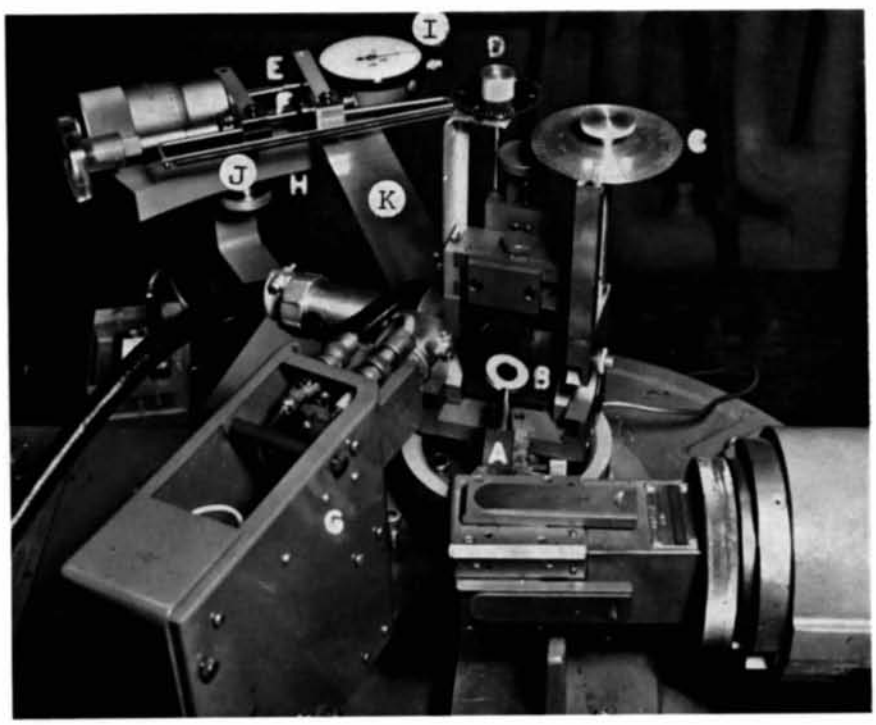

Fig. 2. Photograph of the apparatus used in the stress measurement of the two-plane method.

[*To face p.* 580

tilted by various arbitrary angles about the X axis, the minimum can be found where $\Delta\varphi^0$ is zero. The existence of the minimum was experimentally verified.

The quantity, $\Delta\chi^1$ had to be determined to calculate the alignment error of the plane $(h_1k_1l_1)$. As shown in Fig. 1, $\Delta\chi^1$ is the angle between OX (X axis) and OX^1, the zone axis of the planes $(h_1k_1l_1)$ and $(h_0k_0l_0)$. The quantity, $\Delta\chi^1$ was determined by measuring the Bragg angle, θ^1 and then tilting the crystal to an angle, $-\alpha$ which brought another plane of the $\{h_1k_1l_1\}$ family in a diffracting condition and gave the Bragg angle value θ^{-1}. As derived in the Appendix,

$$\Delta\chi^1 = \frac{\theta^1 - \theta^{-1}}{2\sin\alpha}. \tag{13}$$

The error due to the crystal surface not coinciding with the diffractometer axis was eliminated by finding the position where ΔZ [equations (9) and 10)] was zero. This position was determined by measuring $2\theta^0$ and $2\theta^1$ at various positions of Z. When the values of the lattice parameter, a_0 were plotted against Z, the graph like that shown in Fig. 3 resulted. The intersection of the lines shows the true value of a_0 and where ΔZ is zero. In the experiment, where the data for Fig. 3 were determined, $(h_0k_0l_0)$ was the tenth order reflection of the (001) plane of a copper crystal. There were two $(h_1k_1l_1)$ planes which have θ values close to each other, namely the third order of (113) and the fourth order of (112). It is seen that all three curves intersect at the same value of Z. Correcting for ΔZ is quite tedious. When θ rocking scans are performed, the deviation, ΔZ causes the diffracted X-rays to strike the counter window in a different place. However, as long as the range of angles over which the diffracted intensity rises above background can be received, and the sensitivity of the counter is uniform, which it was, no shift in the Bragg angle results. Therefore, this procedure was preferred.

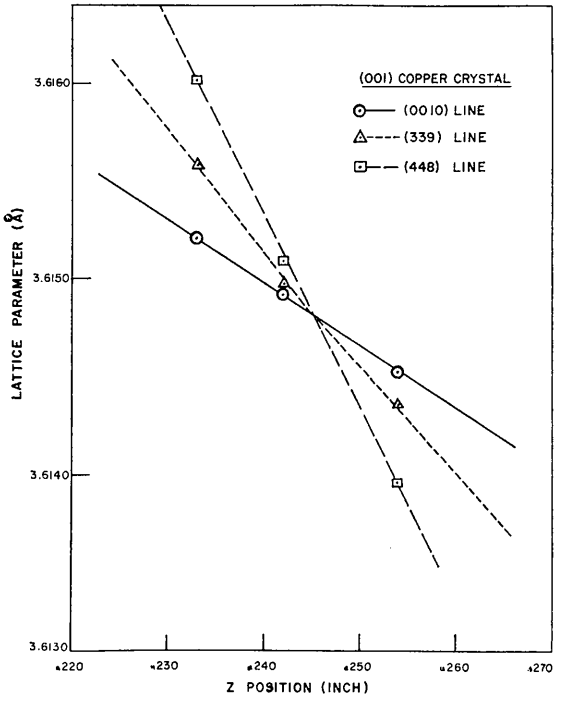

Fig. 3. Diagram showing the determination of the Z_0 position ($\Delta Z = 0$).

Comparison of results from the two-plane method and other techniques

Most of the experiments to determine the stresses by the two-plane method were performed with copper crystals. The original objective of this study was to determine the origins of stresses in electrodeposits. Single-crystal electrodeposits were chosen because the numerous studies of polycrystalline ones had failed to elucidate the phenomena involved in internal stresses. It was decided to electroplate copper because it was known how to produce single crystals and the process is relatively free of complicating side reactions. The substrate was a cylindrical copper single crystal. It was mounted in Teflon so that only the plane perpendicular to the cylindrical axis was exposed. Copper was deposited on this plane, which was close to (001), from a normal solution of copper sulfate and sulfuric acid. The solution was prepared with distilled water and chemically pure reagents and treated with activated charcoal to remove organic contaminants. Deposition at low current density to remove metallic impurities preceded plating on the single crystals. The stresses and lattice parameters of the substrate were determined by the two-plane method. The $(h_0k_0l_0)$ plane was (0,0,10) and the $(h_1k_1l_1)$ was (339). These high-order reflections were obtained by using molybdenum radiation. The $[1\bar{1}0]$ direction was the tilting axis. Therefore, the stresses were calculated on the basis of equal biaxial stress in $\langle 110\rangle$ directions. The substrate was briefly electropolished to clean the surface prior to copper plating. After plating, the stress and lattice parameter were determined again. One copper crystal of high perfection was used only as a stress-free standard. The results of the various tests are listed in Table 1. The stress and lattice-parameter values were calculated in each case from both the center of gravity of the diffraction curve and the maximum point of the parabola. A few data calculated using the intensity maximum are also included. It is seen that the calculated stresses in the stress-free standard, the substrate and the deposits are all of the same order of magnitude regardless of how the value of the Bragg angle was obtained from the diffraction curve. The deposits are therefore stress free within the experimental error of about $\pm$ 1000 psi. This result was confirmed by plating single crystals of copper under the same conditions on a thin-sheet substrate, so that the stresses could be measured during deposition by a mechanical device. A description of the device and the results have been published elsewhere (Schneider & Weil, 1968).

Table 1. *Stress and lattice parameters of copper crystals*

Specimen	Calculations using center of gravity		Calculations using the parabolic maximum	
	Stress (psi)	a_0(Å)	Stress (psi)	a_0(Å)
Stress-free standard, test 1*	−700	3·6152	300	3·6152
Stress-free standard, test 2	−600	3·6152	500	3·6152
Substrate, test 1	300	3·6156	100	3·6154
20μ deposit	−100	3·6155	100	3·6148
Substrate, test 2	700	3·6154	300	3·6153
20μ deposit	0	3·6150	−300	3·6148
Substrate, test 3	−600	3·6154	−100	3·6153
60μ deposit	−500	3·6147	−1100	3·6148

* Intensity maximum yielded −600 psi and 3·6152 Å.

Some experiments were conducted with 3000 Å-thick nickel single crystals epitaxically vapor deposited onto (001) cleavage faces of potassium chloride. The KCl crystals were heated to 400 °C and nickel was deposited at a rate of about 15 Å per second. The X-ray measurements were performed at room temperature while the nickel still adhered to the substrate. The stresses determined by the two-plane method were compared with those obtained by the procedure used by Freedman (1962), where the stresses in the vapor deposit were calculated from the shift in the Bragg angle with respect to those of the substrate, which was assumed to be stress free. It was assumed by Freedman that the respective crystal planes of deposit and substrate are parallel and that all shifts in the Bragg angle are due to stress and that the lattice parameter of the vapor deposit is the same as that of the bulk metal. As the diffraction curves obtained by using molybdenum radiation were too weak to be usable because of the thinness of the nickel film, a copper tube was used. Therefore, it was not possible to obtain diffraction curves from high-order planes with approximately the same Bragg angle, which would have been desirable. The (111), (002), (022) and (113) diffraction curves were determined using both the 2θ-scanning and θ-rocking techniques. The stresses and lattice parameter were calculated by the two-plane-method equations where $(h_0k_0l_0)$ was (002) and $(h_1k_1l_1)$ either (111), (022) or (113). As the (111) and (113) planes are brought into diffracting conditions by tilting about a $\langle 110 \rangle$ type axis in the plane of the deposit and the (022) planes by tilting about $\langle 100 \rangle$, the stresses which are listed in Table 2 are in these directions, as indicated. The calculations were made assuming an equal biaxial stress state. It can be seen from Table 2 that the average stress values obtained from the θ-rocking data and θ–2θ scanning agree quite well. There is some scatter in the individual values in both cases although less when θ-rocking data were used. Some of the errors are reflected in the lattice-parameter values which should, of course, be the same regardless of which $(h_1k_1l_1)$ plane was used. The stresses calculated from the angular shift of the nickel lines with respect to those of the potassium chloride substrate show more scatter and, in general, are higher than those determined by the two-plane method. There is also less agreement between the stress values calculated from data obtained by θ–2θ scanning than by θ rocking. However, the values determined by the two-plane method and Freedman's method agree at least about the order of magnitude of the stresses present in the nickel films. A further check of the stress values can be made by assuming that the nickel film was stress free at the temperature at which it was deposited, namely 400 °C. The stresses then resulted on cooling to 25 °C and were due to the difference in the coefficients of thermal expansions of nickel and potassium chloride. These stress values again are of the order of 10^5 psi. Such stresses exceed the yield strength of bulk nickel. Freedman suggested that thin films possessed much higher yield strength, however.

A third comparison of stress values obtained by the two-plane method was made with those determined by the use of electrical strain gages. For this experiment, a niobium single crystal was selected because of its relatively high yield point. A compression fixture was constructed which fitted in the specimen holder used in the other experiments. The fixture contained a screw device to compress the crystal. The surface of the niobium crystal was the (011) plane. The $(h_1k_1l_1)$ plane tilted

Table 2. *Stress values*

Stresses and lattice parameters calculated by two-plane method of nickel films on potassium chloride

Plane		Direction	θ–2θ scanning		θ-rocking curve	
$h_0k_0l_0$	$h_1k_1l_1$	of stress	σ(kpsi)	a_0 (Å)	σ(kpsi)	a_0 (Å)
(002)	(111)	$\langle 110 \rangle$	−212	3·5258	−169	3·5301
(002)	(022)	$\langle 100 \rangle$	−119	3·5383	−149	3·5328
(002)	(113)	$\langle 110 \rangle$	−150	3·5341	−177	3·5291
Average			−160	3·5327	−165	3·5307

Stresses determined from Bragg-angle shift of nickel films with respect to Bragg angle of KCl (Freedman's Method)

Miller indices of nickel plane	Calculated stress (kpsi) from θ–2θ scanning data	Calculated stress (kpsi) from θ-rocking curve data
(111)	−136	−50
(002)	−270	−260
(022)	−763	−272
(113)	−339	−276
Average	−457	−214

into position for the two-plane method was (411). As the sixth-order diffraction curve of (110) and the second order of (411) occur at the same Bragg angle, these two planes were selected for the two-plane-method measurements. The positions of the Bragg angles of the two planes were determined before and after straining. Three such experiments were performed. In each experiment, a different force was imposed by the screw mechanism on the crystal in the $[1\bar{1}0]$ direction and measured with strain gages. The stresses calculated by the two-plane method were in the $[3\bar{3}2]$ direction because of the planes used. The strain gage yielded values in the $[1\bar{1}0]$ direction. These values, shown in Table 3(*a*), when converted into strains in the $[3\bar{3}2]$ directions are somewhat higher than those calculated by the use of the two-plane method. Again some of the stresses are reflected in changes in the lattice parameter. If it is assumed that the lattice parameter does not change so that the stresses are calculated from the difference between the Bragg angle before and after compression, the agreement between the strain-gage values and those from the X-ray data is very good as shown in Table 3(*b*). However, as already pointed out, the assumption of a constant and known lattice parameter can only be made in a few special experiments such as the straining of the niobium crystal in the X-ray unit.

Discussion

It is evident that the main reason for the difference between the stress values determined by the three independent ways and those calculated by using the two-plane method is the uncertainty about the lattice parameter. If the value of a_0 is known in the unstressed state and does not change as a result of the conditions which cause the stress, agreement between the X-ray method and the others is good as seen from the experiment with the niobium crystal. When a_0 in the unstressed state is known, a major source of error due to having to tilt can be eliminated. The strain can be calculated then from the difference in the Bragg angle determined from the plane essentially parallel to the surface and that calculated from the known value a_0. In most experiments, however, the lattice parameter in the unstressed state is not known and, for example, in the case of electrodeposits the inclusion in the lattice of foreign substances which cause the stress also can change a_0 (Schneider & Weil, 1968). If the wrong lattice parameter is assumed, considerable error can result. In this case, it would be preferable to determine it by the two-plane method. The results of the experiments which involved the nickel films, indicate that more consistent results can be obtained by using the two-plane method, than Freedman's procedure where the lattice parameter is assumed to be that of bulk material. The fact that some errors result in the lattice parameter and stress values as calculated by the two-plane method if the wrong state of stress is assumed, does not speak against the validity of the procedure. Similar errors result under the same conditions in the well-established X-ray stress-determination method which is used for polycrystalline materials. The uncertainty about the state of stress in single crystals can be diminished by making additional measurements in several directions. Even then some uncertainty remains because even the generally made assumption of plane stress has been shown to be wrong by Palatnik, Fuks & Koz'ma (1965) under certain conditions. They found that there were stresses perpendicular to the surface in layers beneath it. These stresses, which went to zero at the surface, still affected the Bragg-angle value. To eliminate all errors is often too time consuming. Obviously, the more care is taken to determine the state of stress, the better will be the accuracy of the stress and lattice-parameter values. The two-plane method as used in the studies described in this paper was a compromise between the accuracy of stress values and many determinations such as to make the experiments too time consuming. The experiments previously described indicate that the accuracy of stress values obtained by the two-plane method is within an acceptable range. The agreement with stress values determined by other means appears to show the validity of the two-plane method.

While some compromise was made so that the two-

Table 3. *Stresses and lattice parameters of niobium crystal*

(*a*) Comparison of strain-gage and two-plane-method stresses

	Strain-gage results		Two-plane-method results			
			After compression		Before compression	
Test number	Stress, σ_S in [110] (kpsi)	Stress, σ_S in $[3\bar{3}2]$ (kpsi)	a_0 (Å)	Stress, σ_S in [332] (kpsi)	a_0 (Å)	Stress, σ_S in $[3\bar{3}2]$ (kpsi)
1	−14·5	−7·2	3·3017	−6·1	3·3009	0·17
2	−11·9	−6·9	3·3016	−5·1	3·3009	0·26
3	−9·5	−4·7	3·3014	−3·9	3·3009	0·17

(*b*) Comparison of strain-gage and Bragg-angle-shift strains

	Strain-gage measurements			X-ray measurements			
	Measured	Calculated		Measured		Calculated	
Test number	Strain in $[1\bar{1}0]$	Strain in [110]	Strain in [411]	$\Delta\theta_{(660)}$	$\Delta\theta_{(822)}$	Strain in [110]	Strain in [411]
1	−0·001100	0·000446	0·000055	−0·057°	−0·009°	0·000450	0·000071
2	−0·000900	0·000365	0·000045	−0·045	−0·006	0·000354	0·000047
3	−0·000720	0·000292	0·000036	−0·035	−0·004	0·000275	0·000031

plane method is not too cumbersome, further simplification appears not to be warranted. The consideration of the errors resulting from misalignment cannot be neglected. For example, neglecting a 1° error in the vertical misalignment ($\Delta\varphi^0$) of the ($h_0k_0l_0$) plane results in a fictitious stress of 7000 psi in copper crystals when studied as described before. Neglecting an error of 1° in the horizontal misalignment results in a fictitious stress of 38000 psi in the same type of specimen. The need for the special equipment to measure the Bragg angle, the step counting, the control of the room temperature and a well collimated beam can be similarly justified. On the other hand, calculations of the effect of changes in the Lorentz–polarization factor over the angular range studied and of absorption indicated that they can be neglected.

It has already been pointed out that handbook values of the modulus of elasticity and Poisson's ratio of polycrystalline materials should not be used to convert the strains, which are the measured quantities, to stresses. The value of Young's modulus as calculated from the compliances by equation (6) varies for a relatively isotropic crystal like niobium from $1{\cdot}12\times10^7$ psi to $2{\cdot}22\times10^7$ psi. The variation for nickel crystals is from 2×10^7 psi to $4{\cdot}4\times10^7$ psi. Poisson's ratios calculated by using equation (9) vary similarly with crystallographic direction. If the constants, b for equations (4) and (5) are not calculated on the basis of elastic constants for the particular direction under consideration the errors in the stress values can be greater than the standard deviation of the data obtained in the previously described experiments.

The results from the experiments conducted in connection with this study indicate that it is preferable to use the θ-rocking curve rather than θ–2θ scanning. Not only is there no need for ΔZ correction [equations (9), (10)] in the case of the former, but as shown in Table 2, the results are more consistent. However, it is not certain that these advantages justify obtaining the special attachment needed to measure θ with the required accuracy. As conventional scanning curves can be performed with any standard X-ray unit, only the special sample holder would be needed. The results shown in Table 1 as well as some others indicate that using the center of gravity of the diffraction curve as the value of the Bragg angle gives more consistent results than the parabolic maximum or the angle where the intensity is a maximum. Especially where diffraction curves are asymmetric, use of the center of gravity yields the best results.

In conclusion, it is hoped that the publication of this method for determining stresses in single crystals by X-ray diffraction without elaborate additional equipment will encourage investigators to use it. In this way, it is hoped that the method will be developed further and that if there are some inconsistencies, they will manifest themselves.

This paper is based on a thesis submitted by S'Keng Pan to the faculty of the Stevens Institute of Technology in partial fulfillment of the requirements for the Ph. D. degree. The work was supported by the American Electroplaters' Society, Inc. and their permission to publish it is gratefully acknowledged. The authors thank the other members of the Doctoral Committee, Professors Gela, Smith and Gennaro and the AES Project Committee, Messrs Brenner, Cupp, Hardesty, Max, Seyb and Wesley as well as Messrs Bond and Barnes of Bell Telephone Laboratory and Professor Weissmann of Rutgers University for their helpful suggestions and discussions. The permission to use some equipment at the U.S. Steel Research Laboratory in Monroeville, Pa. is also gratefully acknowledged.

APPENDIX

In equations (7) to (10) the changes in the Bragg angles due to alignment errors of the normal and inclined planes are given. As there may be some interest in the derivation of these equations, they are therefore presented here.

The horizontal and vertical components of the angle between the specimen surface and the plane ($h_0k_0l_0$) cause a shift in the Bragg angle as seen from equation (7). The horizontal component, $\Delta\theta_i^0$, shown in Fig. 1, is calculated from equation (11).

The vertical component, $\Delta\varphi^0$ of the angle between the specimen surface and ($h_0k_0l_0$) also affects the value of θ^0 because as a result of it the plane determined by the incident and diffracted X-ray beams is not parallel to the diffractometer plane as illustrated in Fig. 4. The plane determined by the incident beam, BO and the diffracted beam, OD' makes an angle, β with the XZ plane, which is the diffractometer plane and also contains the direction BO. The normals to ($h_0k_0l_0$) and the specimen surface are OZ' and OZ, respectively. Therefore the vertical and horizontal components of the

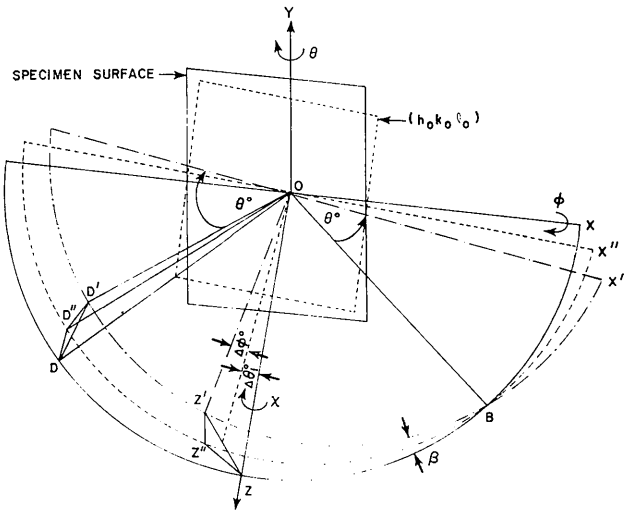

Fig. 4. Diagram showing the angular relationships between the plane ($h_0k_0l_0$) and the specimen surface.

angle ZOZ' are the same as those of the angle between $(h_0k_0l_0)$ and the specimen surface, namely $\Delta\varphi^0$ and $\Delta\theta_i^0$. However, as the point D is further from B than Z, the horizontal component of the angle DOD' is greater than $\Delta\theta_i^0$. This additional change in the Bragg angle is $\Delta\theta_{ii}^0$. The value of $\Delta\theta_{ii}^0$ thus depends on $\Delta\varphi^0$ and θ^0. An equation for calculating this relationship can be derived by considering that

$$\beta \simeq \sin\beta = \frac{Z'Z''}{BZ''} = \frac{R\Delta\varphi^0}{R(\pi-2\theta)/2} = \frac{2\Delta\varphi^0}{\pi-2\theta}, \quad (14)$$

where R is the radius of the diffracting circle and Z'' is the projection of Z' on the XZ plane. The angles β and ZOZ' are small so sines can be set equal to angles and arcs to chords. If $\Delta\varphi^0$ were zero, the diffracted beam lying in the XZ plane would be in the direction OD. If D'' is the projection of D' on the XZ plane, it can be seen from Fig. 4 that

$$\cos\beta = \frac{D''B}{D'B} = \frac{R(\pi-2\theta^0)-R(\Delta\theta_{ii}^0)}{R(\pi-2\theta^0)} = 1-\frac{\Delta\theta_{ii}^0}{\pi-2\theta_{ii}^0}. \quad (15)$$

Again, because β is a small angle, only the first two terms of the cosine series need be considered. Substituting the value of β from equation (14) into (15),

$$1-\tfrac{1}{2}\left[\frac{2\Delta\varphi^0}{\pi-2\theta^0}\right]^2 = 1-\frac{\Delta\theta_{ii}^0}{\pi-2\theta^0} \quad (16)$$

and

$$\Delta\theta_{ii}^0 = \frac{(\Delta\varphi^0)^2}{(\pi/2)-\theta^0}. \quad (17)$$

By using the value of θ^0 obtained according to equation (11), the error, $\Delta\theta_i^0$ is eliminated, then the only alignment error in equation (7) is $\Delta\theta_{ii}^0$.

Errors can result in alignment of the inclined plane $(h_1k_1l_1)$ because the X axis does not coincide with the zone axis of the planes $(h_0k_0l_0)$ and $(h_1k_1l_1)$. As can be seen in Fig. 1, the angle between $(h_0k_0l_0)$ and $(h_1k_1l_1)$ is α and their zone axis is OX^1. The X axis, OX makes an angle $\Delta\chi^1$ with OX^1 which results in a Bragg-angle shift. There is also an error because of the already discussed angle between the specimen surface and the $(h_0k_0l_0)$ plane as the true zone axis naturally lies in this plane. The error, $\Delta\theta_i^1$ consisting of two terms results. The change in the Bragg angle before tilting was $\Delta\theta_i^0$. After tilting OX by an angle, α, the change becomes $(\Delta\theta_i^0\cos\alpha)$. As the tilting is not performed about the true zone axis, OX^1, a second error, $(\Delta\chi^1\sin\alpha)$ is introduced. Thus

$$\Delta\theta_i^1 = \Delta\theta_i^0\cos\alpha + \Delta\chi^1\sin\alpha \quad (18)$$

Another error, $\Delta\theta_{ii}^1$ results because by tilting about OX by a quantity α, the actual angle between the planes, $(h_0k_0l_0)$ and $(h_1k_1l_1)$ becomes α'. The angles, α and α' are related by

$$\alpha' = \alpha\cos\Delta\chi^1. \quad (19)$$

Considering again only the first two terms of the cosine expansion,

$$\Delta\alpha = \alpha'-\alpha = -\tfrac{1}{2}\alpha(\Delta\chi^1)^2. \quad (20)$$

The change in the Bragg angle is again due to the fact that the diffracted beam is inclined to the plane of the diffractometer by an amount $\Delta\varphi^0+\Delta\alpha$. Thus, similarly to equation (17),

$$\Delta\theta_{ii}^1 = \frac{(\Delta\varphi^0+\Delta\alpha)^2}{(\pi/2)-\theta^1} = \frac{[\Delta\varphi^0-(\alpha/2)(\Delta\chi^1)^2]^2}{(\pi/2)-\theta^1}. \quad (21)$$

If terms of higher order in small angles are neglected,

$$\Delta\theta_{ii}^1 = \frac{(\Delta\varphi^0)^2-\alpha\Delta\varphi^0(\Delta\chi^1)^2}{\pi/2-\theta^1}. \quad (22)$$

The total Bragg-angle change is, therefore,

$$\Delta\theta_i^1+\Delta\theta_{ii}^1 = \Delta\chi^1\sin\alpha+\Delta\theta_i^0\cos\alpha + \frac{(\Delta\varphi^0)^2-\alpha\Delta\varphi^0(\Delta\chi^1)^2}{(\pi/2)-\theta^1} \quad (23)$$

which is identical to equation (8).

As already indicated, the quantity $\Delta\chi^1$ can be determined from a second measurement of the Bragg angle, θ^1 when the crystal is tilted by the angle, $-\alpha$ which brings another plane of the $\{h_1k_1l_1\}$ family into a diffracting condition. Then the changes in the Bragg angle,

$$\Delta\theta_{ii}^{-1}+\Delta\theta_i^{-1} = \frac{(\Delta\varphi^0)^2+\alpha\Delta\varphi^0(\Delta\chi^1)^2}{(\pi/2)-\theta^1} - \Delta\chi^1\sin\alpha+\Delta\theta^0\cos\alpha. \quad (24)$$

It has been found experimentally that the error $\Delta\theta_{ii}^1$ is fairly small and can be neglected for this calculation. Thus, substracting equation (24) from (23),

$$\Delta\theta_i^1-\Delta\theta_i^{-1} = 2\Delta\chi^1\sin\alpha, \quad (25)$$

allowing the magnitude of $\Delta\chi^1$ to be determined.

References

BURKE, J. & TOMKEIEFF, M. W. (1968). *Acta Cryst.* A**24**, 683.

ELLIS, T., NANNI, L. F., SHRIER, A., WEISSMANN, S., PADAWER, G. E. & HOSOKAWA, N. (1964). *J. Appl. Phys.* **34**, 3364.

FREEDMAN, J. F. (1962). *J. Appl. Phys.*, **33**, (Suppl.), 1148.

GREENOUGH, G. B. (1955). *X-ray Diffraction by Polycryst alline Materials* p. 608. Edited by H. S. PEISER, H. P. ROOKSBY & A. J. C. WILSON, London: *Institute of Physics.*

IMURA, T. (1954). *Bull. Naniwa Univ. (Japan)*, A**2**, 51.

IMURA, T. (1957). *Bull. Univ. Osaka Pref. (Japan)*, A**5**, 99.

IMURA, T., WEISSMANN, S. & SLADE, J. J. (1962). *Acta Cryst.* **15**, 786.

NEWTON, C. J. (1964). *J. Res. Nat. Bur. Stand.* **67**C, 249.

PALATNIK, L. S., FUKS, M. YA. & KOZ'MA, A. A. (1965). *Phys. Met. Metallogr.* **20**, 753 (In Russian).

SCHNEIDER, R. & WEIL, R. (1968). *Plating*, **55**, 1063.

SLADE, J. J., WEISSMANN, S., NAKAJIMA, K. & HIRABAYASHI, M. (1964). *J. Appl. Phys.* **35**, 3373.

TEGART, W. J. MCG. (1966). *Elements of Mechanical Metallurgy*, New York: MacMillan.

WASILEWSKI, R. J. (1955). *J. Phys. Chem. Solids*, **26**, 1643.