Application of the Energy-Dispersive X-ray Diffraction Method to Determine Static and Dynamic Displacements Close to D in Ta Single Crystals

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Abstract

The energy-dispersive X-ray diffraction method has been used to measure integrated Bragg intensities from TaDₓ single crystals as a function of D concentration and scattering vector. The observed attenuation can be described in terms of a thermal and a static Debye-Waller factor (DWF). From the static DWF, for small scattering vectors, the displacements \( u_1 = 0.095 (5) \) Å of the four Ta atoms closest to the D atom are obtained and, for large scattering vectors, the change of the mean-square thermal displacement of these atoms \( \Delta v_1^2 \approx -[5.5 (3)] \times 10^{-4} \) Å².

I. Introduction

Since energy-dispersive X-ray diffraction was introduced (Giessen & Gordon, 1968; Buras, Chwasczewska, Szarras & Szmid, 1968), it has been applied to various problems. The method can be used for powder measurements (Chwasczewska, Szarras, Szmid & Szymczak, 1971; Szpumar, Ojanen & Laine, 1974) and for single-crystal investigations (Buras, 1971; Fucksamachi, Togawa & Hoseya, 1973; Skelton, Radoff, Bolsahtis & Verbalis, 1972; Buras, Olsen, Gerward, Selsmark & Lindegaard-Andersen, 1975; Skelton, 1976; Sakamaki, Hosoya & Inkamaki, 1980). As the details of the method have been extensively reported (Buras, 1971; Fucksamachi, Togawa & Hoseya, 1973; Skelton, Radoff, Bolsahtis & Verbalis, 1972; Buras, Olsen, Gerward, Selsmark & Lindegaard-Andersen, 1975; Skelton, 1976; Sakamaki, Hosoya & Inkamaki, 1980), we describe in this paper only the advantages with regard to its application to the Debye-Waller-factor (DWF) measurements of D in Ta single crystals (\( \alpha \) phase), i.e. we are interested in the relative change of Bragg intensities due to thermal and static displacements at high scattering vectors. As the Bremsstrahlung is used, photon energies up to 50 keV are obtained and thereby we are able to reach twice the order of reflection compared with the angular dispersive method (using Mo K\( \alpha \) radiation).

II. Theoretical background

The attenuation of Bragg-scattering intensities due to deviations \( \delta R_s \) of atoms from their average position in a lattice can be described by a DWF which is given by

\[
I_{\text{Bragg}} \propto \langle \exp (iK\cdot \delta R_s) \rangle^2 \equiv \exp (-2M).
\]

K is the scattering vector and \( \delta R_s \) is the total displacement of the atom \( s \). If point defects are present \( \delta R_s \) is given by the sum of static and thermal displacements. The averaging procedure (\( \langle \cdot \rangle \) means time average and — volume average) in this case induces a coupling between the static and thermal displacements (Krivoglaz, 1959, 1969). This effect originates from the deviation of the probability distribution of the thermal displacements from a Gaussian distribution if randomly distributed point defects are present in the

From these measurements we get information on the mean-square thermal displacements (m.s.t.d.) of the average Ta lattice, the static displacements of the Ta atoms nearest to the D and the change of the m.s.t.d. of these Ta atoms compared with the rest of the host-lattice atoms. The information on the local thermal vibrations close to a D (point defect) has been shown to be due to the non-linear coupling of static and thermal displacements (Krivoglaz, 1969; Metzger, Behr, Steyrer & Peisl, 1983; Metzger, Steyrer, Behr & Peisl, 1983).

It is the aim of this paper to show that the energy-dispersive method is ideally suited for this kind of measurement since the coupling effect appears only for high scattering vectors and only relative intensity measurements are required. We will describe the experimental procedure of the measurement of the static and thermal Debye-Waller factor (DWF) in detail. First, we review the theoretical results as to the appearance of the coupling effect in the DWF of Bragg intensities from lattices containing point defects (§ II). In § III the energy-dispersive method will be described together with the details of the sample preparation of TaD single crystals. The data evaluation as applied to deduce the thermal and static DWF will be given in § IV and finally the results and the interpretation will be displayed and discussed in the last section.

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lattice. The coupling effect has been shown to be a function of about $K^{-4}$ (Krivoglaz, 1959) and causes an interdependence of the static and the thermal DWF at high $K$ values (Behr, Metzger & Peisl, 1983). Although this theory is rather old it has not been verified experimentally until recently (Metzger, Steyerer, Behr & Peisl, 1983). In this paper we applied the Krivoglaz theory to point defects (H or D atoms), randomly distributed on the tetrahedral sites of the b.c.c. lattice of Ta, and showed that the static DWF and the coupling term are mainly determined by the static and thermal displacements of the host-lattice atoms very close to the point defect. In the cases of H (D) in Nb or Ta, for instance, (Metzger, Behr, Steyerer & Peisl, 1983) the total DWF is given by

$$M = M^{th} + L^*$$

$$L^* = (4/3)c \left(1 - \cos K \cdot u_1\right) (1 - \frac{1}{2} K^2 A\nu_1^2). \tag{2}$$

$M^{th}$ is the thermal DWF which is determined by the m.s.t.d. $\langle u^2 \rangle$ of all lattice atoms. The concentration-dependent second term in (2) denotes the static DWF exponent $L = (4/3)c \left(1 - \cos K \cdot u_1\right)$ (Metzger, Behr & Peisl, 1982) and the coupling term $- (1/2) K^2 A\nu_1^2$. Here $A\nu_1^2$ gives essentially the difference between $\langle u^2 \rangle$ and the m.s.t.d. of the atoms of the first atomic shell around H(D). $u_1$ is the static displacement of these atoms due to an individual H(D) atom. For small $K$ the coupling term can be neglected and thermal and static DWF are independent because the corresponding displacements can be treated as independent. Only for high values of $K$ can the coupling term be expected to play a role. Therefore, the measurements of integrated Bragg diffraction intensities as a function of the defect concentration up to high values of the scattering vector will give detailed information about the static and the thermal displacements close to point defects by applying the aforementioned theory to the experimental data. The thermal DWF $M^{th}$ is insensitive to the coupling effect for reasons given elsewhere (Metzger, Steyerer, Behr & Peisl, 1983).

### III. Experimental details

#### Fixed single-crystal method

The Bragg law for a fixed single crystal and a detector angle $2\theta$ can only be solved if the vector normal to a specific set of lattice planes bisects the incident and diffracted X-ray beam and an appropriate wavelength (energy) is available from the continuous Bremspectrum. For a cubic crystal the Bragg law can be written as

$$E_n a_0 \sin \theta = n \times 6.199 \text{ (keV Å)} \tag{3}$$

where $a_0$ is the lattice parameter, $\theta$ the scattering angle and $E_n$ is the photon energy (in keV) as selected by the order $n$ of the reflection. For each given crystal orientation in the position of reflection, the selected energy values $E_n$ have the same distance (e.g., in the case of the crystal orientation $<110>$, $n$ becomes $n = k\sqrt{2}$, where $h=k$ are the Miller indices). The energies $E_n$ are directly proportional to the reciprocal-lattice vectors

$$|G| = 2\pi n/a \quad [n = (h^2 + k^2 + l^2)^{1/2}].$$

The energy-dispersive method determines the scattering vector $K = k - k_0$ (Fig. 1) to run parallel to the direction of $G$ in reciprocal space, since $K = G$ for Bragg reflection must be fulfilled. For a given range of wavevectors $(2\pi/\lambda_{max} \leq k_0 \leq 2\pi/\lambda_{min})$ the maximal scattering vector $K$ to be reached can be chosen by selection of the scattering angle $\theta$. According to (3), the number of accessible Bragg reflections ($K = G$) can be increased by increasing $\theta$. Thus, the method is very flexible with regard to the number of Bragg reflections of interest. The energy of the diffracted beam will be detected by a solid-state detector with high energy resolution and subsequently recorded in a multichannel analyser (MCA). Here we used an intrinsic Ge counter (Ortec) and a multichannel analyser (Canberra) with 1024 channels.

**Measurement of integrated Bragg intensities**

In the case of the energy-dispersive method the integrated Bragg intensities from a single crystal are obtained by an integration over energies (wavelengths), where

$$\Delta\lambda/\lambda = - \Delta E/E = \cot \theta \Delta \theta. \tag{4}$$

The angular width $\Delta \theta$ is given by the convolution of the divergence $\varepsilon$ of the incident beam and the mosaic spread $\tau$ of the single crystal. Usually $\varepsilon$ is kept very small by a divergence slit $D$ (Fig. 2) and $\Delta \theta$ is given only by the angle $\tau$ of the mosaic spread. In contrast to the angular-dispersive method (e.g. Bragg–Brentano focusing), the beam geometry is not convergent. Each mosaic block in the crystal will pick up the appro-
appropriate wavelength from the white spectrum and the corresponding diffracted beam will appear in a direction given by the $\theta:2\theta$ condition. The angular width of the diffracted beam is $\Delta \theta = 2\tau$. In order to gather the total Bragg diffracted intensity the detector slit has to be wide open ($\sim 6$ times $\tau$). For crystals under consideration in this work ($\tau < 0.2^\circ$) the corresponding energy resolution $\Delta E/E$ (equation 4) is still one order of magnitude smaller than the best energy resolution as given by the detector in the most favourable case ($\Delta E/E \approx 10^{-2}$ at 40 keV). Therefore, the choice of the detector slit is not critical. A further opening ($2\theta > 6\tau$) will only worsen the peak-to-background ratio because more thermal diffuse, Compton and fluorescence scattering will be picked up while the Bragg diffraction intensity remains the same.

The integrated Bragg intensity of a single crystal is given in the kinematic approximation in the case of the energy-dispersive method by (Buras & Gerward, 1975)

$$I_{hkl} = I_0(\lambda) d_{eff} N^2 F_{hkl}^2 \frac{p(\theta)}{2 \sin^2 \theta} \exp(-2M).$$

(5)

$I_0(\tau)$ is the incident intensity at various $\lambda$ as given by the Bremsstrahlung spectrum, $A$ is the illuminated sample surface, which depends on the geometry, $d_{eff} = 1/2\mu(\lambda)$ the penetration depth of the X-rays, which varies strongly with $\lambda$, since the absorption coefficient $\mu$ is proportional to $\lambda^3$ between two absorption edges of the sample material. $N^2$ is the number of unit cells per volume, $F_{hkl}^2$ is the structure factor, $p(\theta)$ denotes the polarization factor. For unpolarised incident X-rays $p = \frac{1}{2}(1 + \cos^2 2\theta)$ (Olsen et al., 1978). $\exp(-2M)$ describes the total DWF due to static and thermal displacements in the lattice. As too many quantities in (5) depend upon the wavelength it would be rather tedious to determine $F_{hkl}^2$ and $\exp(-2M)$ absolutely, although it has been shown to be possible (Buras et al., 1975). In our case, however, only relative integrated intensities are of interest and by taking the ratio of two measurements most of the quantities in (5) will be cancelled. In order to determine $\exp(-2M)$ we perform two kinds of measurements.

(i) For the temperature-dependent part of the DWF $2M$ we measure the integrated Bragg intensities of all reflections at two temperatures. The corresponding total DWF is obtained from the intensity ratio $I(T_2)/I(T_2)$.

(ii) The concentration-dependent part of $2M$ is obtained from a similar procedure at constant temperature but by varying the concentration of the defects (here deuterium). In addition, the temperature-dependent measurements have been performed at each concentration with the aim of checking the change of the temperature-dependent part of $2M$ with the concentration. The details of the data evaluation will be given in the next section.

Sample preparation

Ta single crystals with a mosaic spread of about $\tau = 0.1^\circ$ were oriented along the $\langle 110 \rangle$ direction and purified by a degassing procedure at 2670 K under ultra-high-vacuum conditions ($0.13$ pPa). The D loading was carried out at 923 K in pure D atmosphere of the equilibrium pressure corresponding to a concentration of $c = 0.15$ D/Ta (Veleckis & Edwards, 1969). After cooling, the concentration was checked by the weight increase and by the lattice-parameter change, using the calibrating value $\Delta a/a/\text{at} . \% = 4.8 \times 10^{-4}$ (Pfeiffer & Peisl, 1977). As the phase boundary of the homogenous $\alpha$ phase for D in Ta at room temperature is at 0.25 D/Ta (Schober & Wenzl, 1978), we did not perform an in situ loading on the spectrometer (Behr, Metzger & Peisl, 1982), but rather compared the measured intensities of the loaded sample to a different pure Ta crystal, with the same orientation and mosaic spread. The corresponding corrections are discussed in the next section.

IV. Data evaluation

As we are only interested in the attenuation factor $\exp(2M)$ of the Bragg intensities due to static and thermal displacements we have only to measure relative intensity changes and can thereby avoid the difficult problem of absolute intensity determination. The ratio of two measured intensities is according to (5):

$$I_{hkl}^{(1)} / I_{hkl}^{(2)} = \frac{[I_0^{(1)}(\lambda) d_{eff}^{(1)} N^2 F_{hkl(1)}^2 \frac{p(\theta(1))}{2 \sin^2 \theta(1)} \exp(-2M(1))]}{[I_0^{(2)}(\lambda) d_{eff}^{(2)} N^2 F_{hkl(2)}^2 \frac{p(\theta(2))}{2 \sin^2 \theta(2)} \exp(-2M(2))]}^{-1},$$

(6)

where the indices (1) and (2) indicate the measurement of the intensity either at two temperatures or at two concentrations. In both cases the lattice parameter will be changed and the wavelength as picked up for the Bragg diffraction will also be different. Therefore,
all quantities of (6) which depend on the wavelength will still appear as a correction by taking the intensity ratio as shown in (6). These corrections can be neglected or avoided by the following measurements.

(i) Temperature-dependent measurements

The integrated measurements of the Bragg intensities were taken at $T_1 = 358$ K and at $T_2 = 473$ K. The corresponding lattice-parameter change is about $\Delta a/a \approx 10^{-4}$. As $\Delta a/a = \Delta l/\lambda = -\Delta E/E$ (equation 4), the wavelength shift can certainly be neglected and (7) becomes in this case simply

$$\ln \frac{I_1}{I_2} = 2M(T_2) - 2M(T_1).$$

(ii) Concentration-dependent measurements

The lattice-parameter change due to $0.15$ D/Ta has been measured to be $\Delta a/a = 7.2 \times 10^{-3}$, which is about two orders of magnitude higher than the thermal change of $\Delta a/a$ in (i). The corresponding energy shift $\Delta E$ depends on the incident energy $E$ and amounts to 312 eV for $E = 40$ keV. With the energy calibration of the MCA (51 eV channel$^{-1}$) this means a shift of the Bragg peak of about six channels. In this case, the corrections due to the wavelength change in (6) cannot be neglected any more, but (6) is simplified by decreasing the scattering angle by $\Delta \theta = \tan \theta \Delta a/a$ (under the $2\theta$: $\theta$ condition) in the case of the Ta crystal loaded with $0.15$ D/Ta. In this case the Bragg peaks appear at the same energies (channels) as for the pure Ta crystals and again all $\lambda$-dependent quantities in (6) cancel each other. The remaining corrections due to the small shift $\Delta \theta$ of the scattering angle can easily be calculated. The equation as used for the data evaluation in the case of concentration-dependent measurements reduces to

$$\ln \frac{I_1}{I_2} = 2M(c_2) - 2M(c_1) + \ln B(\Delta \theta),$$

where $\ln B(\Delta \theta)$ is the correction due to the angle change.

The combination of the measurements (i) and (ii) has also been performed to detect the temperature-dependent part of $2M$ for the TaD$_{0.15}$ crystal. As will be shown in the discussion this will induce a small correction due to the change of the m.s.t.d. with D concentration. The integrated Bragg intensities were taken from the MCA by use of a background subtraction procedure, integrated in the MCA system (Canberra 3202, series 35). The background is taken from the intensity in the channels sufficiently far away from the Bragg maximum to perform a linear interpolation. The incident intensity of the X-ray beam has been normalized by use of the intensity of the characteristic Ta L$_x$ lines which are excited by the Bremsstrahlung.

V. Results and discussion

Energy spectra

A sealed Mo tube (55 keV, 10 mA) was used to produce the white X-ray spectrum. The Bragg spectrum obtained from a Ta single crystal oriented along $\langle 110 \rangle$ is shown in Fig. 3. The scattering angle for this measurement was $\theta = 45^\circ$, the 12,12,0 reflection corresponds to an energy $E_{12,12,0} = 45.08$ keV, the lowest reflection to $E_{220} = 7.51$ keV. The energy difference between each reflection is $\Delta E_{sh} = 3.76$ keV. As the intensity in Fig. 3 is given on a log scale, the background intensity appears very much exaggerated. For a reflection in the middle of the spectrum (for instance 770) the peak-to-background ratio is about $10^4$ : 1. The total counting time for this spectrum was about 1.5 h.

Besides the Bragg reflections one can see additional lines in Fig. 3 which can easily be identified by purposely misadjusting the single crystal from the geometrical Bragg condition ($\theta:2\theta$) by a small angle ($\Delta \theta \approx 1^\circ$). The resulting background spectrum is shown in Fig. 4. All Bragg peaks have disappeared (together with the escape peak which appeared 9.88 keV $= E_{GeK_x}$ below the 440 reflection in Fig. 3). The remaining lines are either fluorescent lines of Ta, Pb...
(from the slits), Nb (impurity of the Ta sample) or the characteristic lines of the Mo target. Above the Ta L absorption edges at $E_{Ta,L}=9.9$ keV the scattering volume of the crystal is reduced by a factor of about 2.5 owing to the reduced penetration depth.

Inspection of Figs. 3 and 4 shows that the contamination of some Bragg reflections with fluorescent lines is inevitable, e.g. in the case of the 550 reflection. This situation can be improved by the use of a tungsten tube.

Temperature dependence of Bragg intensities

The Bragg spectrum (see Fig. 3) from a Ta and the TaD$_{0.15}$ single crystal has been measured at $T_1=323$ K and at $T_2=473$ K ($\theta=45^\circ$). The net integrated Bragg intensities $I_1/I_2$ for each reflection have been read from the MCA. In Fig. 5 $\ln I_1/I_2=2M(T_2)-2M(T_1)$ is plotted versus $K^2$ from the 220 to the 990 for pure Ta (□) and for the TaD$_{0.15}$ crystal (•). For pure Ta $\Delta 2M$ follows a straight line with $K^2$, which proves that the harmonic approximation is valid even to the highest order of reflection. In this limit $\Delta 2M=K^2\langle u^2 \rangle$ and the m.s.t.d. $\langle u^2 \rangle$ is directly obtained from the slope $2M/K^2$ in Fig. 5. By use of the Debye approximation for high temperatures we can deduce the Debye temperature $\theta_D=255(8)$ K, which corresponds to $\langle u^2 \rangle=5.9(2)\times10^{-3}$ Å$^2$ at 473 K. In the case of the Ta crystal loaded with 15% D Fig. 5 shows a significant deviation of $\Delta 2M$ from the linear increase with $K^2$ at high $K$ values. This may be due to anharmonic effects and is currently being further investigated.

Concentration dependence of Bragg intensities

The integrated Bragg intensity for each reflection has been evaluated as described before from the Bragg spectrum for a pure Ta crystal ($I_o$) and for the TaD$_{0.15}$ crystal ($I_c$) at a constant temperature ($T=293$ K), where anharmonic effects in the thermal DWF are not excited yet. Consequently, the $\ln I_o/I_c$ has been corrected according to (7). The resulting values $2L^*=\ln I_o/I_c$ is displayed in Fig. 6 as a function of $K^2$. The filled points are taken from a measurement at a scattering angle of $\theta=45^\circ$, while the open points stem from $\theta=58^\circ$. Owing to bad statistics, reflections higher than 10,10,0 have not been used. Also included in Fig. 6 is a measurement of the 222 and 444 reflections (•) as taken from the same two Ta crystals in an asymmetric scattering geometry. In this case the [110] direction lying within the sample surface is oriented parallel to the spectrometer axes and the sample table is turned by the angle between the [111] and [110] directions ($\Delta \omega=35.26^\circ$).

In this scattering geometry the [111] direction again bisects the incident and diffracted X-ray beam. Inspection of Fig. 6 shows that $2L^*$ is isotropic for small $K$ and exhibits a strong deviation from the linear increase with $K^2$. The solid line in Fig. 6 is the fit of the data points by the use of the coupling effect (see § 2). Equation (2) has only two open parameters:

\[ u_1=0.095(5) \text{ Å}, \quad \Delta \omega^2=5.5(3)\times10^{-4} \text{ Å}^2; \]

this has been used to explain the lapse of $2L^*$ versus $K^2$. The pure static DWF $2L=(3/4)(1-\cos K\cdot u_1)$ (dashed line in Fig. 6) shows a significant deviation from the measured $2L^*$ values. Thus, only by taking into account the coupling between static and thermal displacements of the Ta atoms close to the D atom are we able to understand the $K$ dependence of $2L^*$. 
Summary

The method of energy-dispersive X-ray diffraction is described for single crystals at a fixed angle. It is shown that this method is especially suited for DWF measurements, where only the relative change of integrated Bragg intensities is of interest. Owing to the high energies of the white X-ray spectrum very high orders of reflections can be reached. In the present paper we reported upon the attenuation of integrated Bragg intensities due to thermal and static displacements in Ta and TaD_{0.15} single crystals of [110] orientation. For high values of the scattering vector K, we observed the coupling of thermal and static displacements. It showed up as a deviation of the concentration-dependent DWF from a linear increase with K^2. A K^4 dependence was observed which has been compared with theoretical predictions. From a fit using the Krivoglaz theory of the DWF we obtain the displacements u_1 of the four Ta atoms closest to the D atom and the change of the mean-square thermal displacements of these atoms \Delta u^2_1.

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References