The authors are indebted to Professor J. M. Cowley and Dr C. F. Woensdregt for helpful discussions, both orally and written, and to Mr A. Ono of the JEOL company for taking the electron micrographs in Figs. 6, 7 and 13, and Mr R. Wessicken of ETH Zürich for this collaboration.

References

Bown, M. G. & Gay, P. (1958). *Z. Kristallogr.* **111**, 1–14.
Cowley, J. M. (1959). *Acta Cryst.* **12**, 367–375.
Grove, T. L. (1977). *Am. Mineral.* **62**, 932–941.
Hashimoto, H., Kumao, A., Endoh, H., Nissen, H.-U., Ono, A. & Watanabe, E. (1975). *Proceedings of the EMAG Conference, Bristol*, pp. 245–250.
Hashimoto, H., Nissen, H.-U., Ono, A., Kumao, A., Endoh, H. & Woensdregt, C. F. (1976). *Electron Microscopy in Mineralogy*, edited by H.-R. Wenk *et al.* pp. 331–344. Berlin: Springer-Verlag.
Jagodzinski, H. & Korekawa, M. (1976). *Z. Kristallogr.* **143**, 239–277.
Jagodzinski, H. & Korekawa, M. (1978). *Phys. Chem. Miner.* **3**, 69–72.
Kitamura, M. & Morimoto, N. (1977). *Phys. Chem. Miner.* **1**, 199–212.
Klein, S. & Korekawa, M. (1976). *Neues Jahrb. Mineral. Monatsh.* **H.2**, 66–69.
Korekawa, M. & Horst, W. (1974). *Fortschr. Mineral.* **52**, 37–40.
Korekawa, M., Horst, W. & Tagai, T. (1978). *Phys. Chem. Miner.* **3**, 74–75.
Korekawa, M. & Jagodzinski, H. (1967). *Schweiz. Mineral. Petrogr. Mitt.* **47**, 269–278.
Lipson, H. (1972). *Optical Transforms*. London, New York: Academic Press.
McConnell, J. D. C. (1974). *The Feldspars*, edited by W. S. Mackenzie & J. Zussman, pp. 478–490. Manchester Univ. Press.
McLaren, A. C. & Marshall, D. B. (1974). *Contrib. Mineral. Petrol.* **44**, 237–249.
Megaw, H. D. (1960). *Proc. R. Soc. London Ser. A*, **259**, 59–78, 159–183, 184–202.
Morimoto, N., Kitamura, M. & Nakajima, Y. (1975). *Proc. Jpn Acad.* **51**, 729–732.
Morimoto, N., Nakajima, Y. & Kitamura, M. (1975). *Proc. Jpn Acad.* **51**, 725–728.
Scherzer, O. (1949). *J. Appl. Phys.* **20**, 20–29.
Tanji, T. & Hashimoto, H. (1978). *Acta Cryst.* A**34**, 453–459.
Toman, K. & Frueh, A. J. (1973*a*). *Z. Kristallogr.* **138**, 337–342.
Toman, K. & Frueh, A. J. (1973*b*). *Acta Cryst.* A**29**, 127–133.
Toman, K. & Frueh, A. J. (1976*a*). *Acta Cryst.* B**32**, 521–525.
Toman, K. & Frueh, A. J. (1976*b*). *Acta Cryst.* B**32**, 526–538.
Wenk, E., Wenk, H.-R., Glauser, A. & Schwander, H. (1975). *Contrib. Mineral. Petrol.* **53**, 311–326.
Wenk, H.-R. (1978). *Proceedings of the 9th International Congress on Electron Microscopy, Toronto*, Vol. 3, pp. 404–419.

Acta Cryst. (1981). A**37**, 238–241

The Observation of Forbidden Reflections in V_3Si*

By Bernard Borie

The Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, *USA*

(*Received* 16 *July* 1980; *accepted* 7 *October* 1980)

Abstract

Structurally forbidden Bragg maxima in the X-ray diffraction pattern of V_3Si have been observed. These reflections are excited by nonspherical electron distributions and anharmonic and anisotropic thermal motion. The forbidden reflections which are accessible to such excitation are correctly predicted by theory. Further studies of such maxima both with neutrons and X-rays should provide insights into the electronic and thermal behaviour of A15 compounds.

* Research sponsored by the Material Sciences Division, US Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

0567-7394/81/020238-04$01.00

Introduction

There has been recent interest in the experimental observation of structurally forbidden Bragg maxima from simple crystals. These very weak reflections have been found in the X-ray patterns of diamond (Bragg, 1921), silicon (Roberto & Batterman, 1970), germanium (Colella & Merlini, 1966), zinc (Merisalo, Järvinen & Kurittu, 1978) and both allotropes of tin (Field, 1976; Bilderback & Colella, 1975). Their measurement is useful because they are direct indications of anharmonic and anisotropic thermal motion and nonspherical electron distributions about nuclei. Though these phenomena are expected to cause small changes in other reflections, the excitation of forbidden maxima is understood to depend on them alone. The static and dynamic effects may be separated by studying the temperature dependence of the reflections, or by combining the results of X-ray and neutron diffraction measurements. We here report the detection of structurally forbidden reflections in the X-ray pattern of V_3Si, which has the important A15 structure (space group $Pm3n$).

From a consideration of the symmetry of an atomic environment, a method (Borie, 1974) has been developed for predicting which of the forbidden maxima may be excited. For the two classes of reflections for which the conventional structure factor vanishes for those compounds with the A15 structure (all indices odd, or one index odd and the other two both even or both odd multiples of two) one finds a single criterion for the possibility of excitation: no two indices may have the same magnitude. According to the method all other structurally forbidden maxima must remain extinguished. For V_3Si, within the limiting sphere for Cu $K\alpha$ radiation ($h^2 + k^2 + l^2 < 38$ approximately) there are only three such reflections: $hkl = 531$, 140 and 340. Note that two of these have companions (the same d spacing), which according to the theory may not be excited: $hkl = 322$ and 500. An observation that they remain extinguished while 140 and 340 are detected confirms both the accuracy of the experimental method and the theory.

Experimental method

A stoichiometric single crystal of V_3Si in the form of a disc approximately 10 mm in diameter and 2 mm thick was used for this work. The surface normal was a 111 direction. Prior to any measurement its surface was etched with a 5% HF, 35% HNO_3, 60% lactic acid solution and washed with alcohol to avoid diffraction effects related to surface contaminants. Diffraction maxima were measured with a conventional General Electric diffractometer and goniometer. The X-radiation was Cu $K\alpha$ from a flat nearly perfect germanium (111) monochromator. A pinhole after the monochromator confined the entire primary beam to the specimen surface. Before any intensity measurement was made the pattern of Renninger double-diffraction maxima to be expected was computed and observed by rotating the specimen about the relevant reciprocal-lattice vector with the specimen and detector at the Bragg position. Care was taken to select a specimen orientation such that no such double-diffraction condition was satisfied. All specimen tilts necessary to satisfy the Bragg condition were made by tilting the specimen normal toward the incident beam to ensure that the specimen intercepted all of the primary radiation.

Count rates were measured with a Si(Li) solid-state detector. Its resolution was 185 eV FWHM at 5·9 kV, its area was 12·3 mm^2, and its effective sensitive depth was 5·28 mm. The diffractometer was scanned in a θ–2θ mode at approximately 0·008° 2θ min^{-1} and the total counts accumulated in 800 s of diffracted Cu $K\alpha$, and of the fluorescent V $K\alpha$ and V $K\beta$ were recorded with the aid of a multichannel analyzer.

Analysis of the fluorescent radiation

The diffracted intensity was converted to absolute units using the fluorescent radiation. Since this method for in effect measuring the incident beam power is novel, we describe it in some detail.

For an incremental volume dv of material containing N_0 atoms per unit volume irradiated by a beam of intensity I_0, the number of photons annihilated by atomic ionization per second is $(I_0/h\nu)N_0\tau_a dv$, where τ_a is the atomic absorption cross section. If the fraction of these which cause K ionization is G_K and the fluorescent yield is W_K, the number of K photons emitted per second is $W_K G_K N_0 \tau_a [(I_0/h\nu)dv]$. Values of these quantities appropriate for Cu $K\alpha$ incident onto V_3Si are:

$$\tau_a = 1{\cdot}971 \times 10^{-24}\ \mathrm{m}^2 \quad N_0 = 5{\cdot}70 \times 10^{28}\ \mathrm{m}^{-3}$$
$$G_K = 0{\cdot}892 \quad W_K = 0{\cdot}253.$$

The atomic absorption cross section and the K-edge jump ratio for vanadium, used to calculate G_K, are from *International Tables for X-ray Crystallography* (1962). N_0 was calculated using $a_0 = 4{\cdot}722$ Å. The fluorescent yield is as given by Bambynek, Crasemann, Fink, Freund, Mark, Swift, Price & Venugopala Rao (1972).

If α is the fraction of K photons emitted which are V $K\alpha$, we find that the volume increment dv irradiated by a beam of Cu $K\alpha$ of intensity I_0 emits (25·354 mm^{-1})$[(I_0/h\nu)\alpha\ dv]$ V $K\alpha$ counts per second. After appropriately modifying this result to account for absorption in the air path and the beryllium window of the counter, and given the solid angle intercepted by the counter face, we find that the detector should measure $[(I_0/h\nu)\alpha\, dv] \times 0{\cdot}002425$ mm^{-1} V $K\alpha$ and $[(I_0/h\nu)(1-\alpha)\, dv] \times 0{\cdot}002621$ mm^{-1} V $K\beta$ counts per second.

If we now replace the infinitesimal sample with a semi-infinite slab such that the incident beam makes an angle $\theta + \varphi$ and the detected fluorescent radiation makes an angle $\theta - \varphi$ with its surface, it is a conventional result that $I_0\, dv$ in the above expressions is replaced by $P_0/[\mu + \mu' \sin(\theta + \varphi)/\sin(\theta - \varphi)]$. Here P_0 is the total Cu $K\alpha$ power incident on the slab, and the sample linear absorption coefficients for Cu $K\alpha$ and the fluorescent radiation are μ and μ'. With the tabulated values of the absorption coefficients for V_3Si, we find that the actual measured count rates $R\alpha$ and $R\beta$ should be

$$R\alpha = \left\{ \frac{0.02425\ P_0/h\nu}{1176.75 + 641.98 \sin(\theta+\varphi)/\sin(\theta-\varphi)} \right\} \quad (1)$$

and

$$R\beta = \left\{ \frac{0.02621(1-\alpha)P_0/h\nu}{1176.75 + 492.60 \sin(\theta+\varphi)/\sin(\theta-\varphi)} \right\}. \quad (2)$$

Measurements of $R\alpha$ and $R\beta$ may be reduced to values of α and $P_0/h\nu$. From several measurements we find $\alpha = 0.894$, in good agreement with Bambynek *et al.* (1972), and for our instrument $P_0/h\nu$ is about 10^8 photons s^{-1}.

Analysis of the coherent scattering

For an infinitesimal sample of volume dv and for a detector sufficiently large to intercept all of the diffracted power P at Bragg angle θ it is an elementary result that

$$\int P\, d\theta = I_0 \left(\frac{e^4}{m^2 c^4} \right) p \frac{\lambda^3 F^2}{v_a^2} dv.$$

The unit-cell volume is v_a and the structure factor F. For a perfect germanium monochromator the Lorentz–polarization factor p is $(1 + 0.89 \cos^2 2\theta)/1.89 \sin 2\theta$. For a semi-infinite slab, as before, we may replace $I_0\, dv$ by $P_0/[\mu + \mu \sin(\theta+\varphi)/\sin(\theta-\varphi)]$. After accounting for absorption in the air path and the detector window, if R_c is the actually observed count rate associated with the Bragg maximum, we find that

$$\int R_c\, d\theta = 3.197 \times 10^{-6} F^2 \left\{ \frac{1 + 0.89 \cos^2 2\theta}{\sin\theta \cos\theta} \right\} \times \left\{ \frac{P_0 \sin(\theta-\varphi)/h\nu}{1176.75 \sin\theta \cos\varphi} \right\}. \quad (3)$$

It is convenient to express the measurements in terms of $R' = R_c/R\alpha$, the ratio of the coherently scattered Cu $K\alpha$ counts to those of the fluorescent V $K\alpha$. Combining expressions (1) and (3) we find that

$$\int R'\, d\theta = 2.2791 \times 10^{-4} F^2 \left\{ \frac{1 + 0.89 \cos^2 2\theta}{\sin^2\theta} \right\} \times (\tan\theta - 0.294 \tan\varphi). \quad (4)$$

Results and discussion

Diffractometer scans for the structurally forbidden maxima hkl = 140, 322, 340, 500 and 531 were performed. As predicted by theory, 322 and 500 remained extinguished. Small maxima for 140 and 340 were found from which we computed, from (4), F_{140} = 0·33 and F_{340} = 0·16 electrons. Typical specimens of our scans are shown in Fig. 1. Though the background in the vicinity of 531 is higher, resulting in a less favorable signal-to-noise ratio, our measurements indicate that the 531 maximum remains unexcited. The

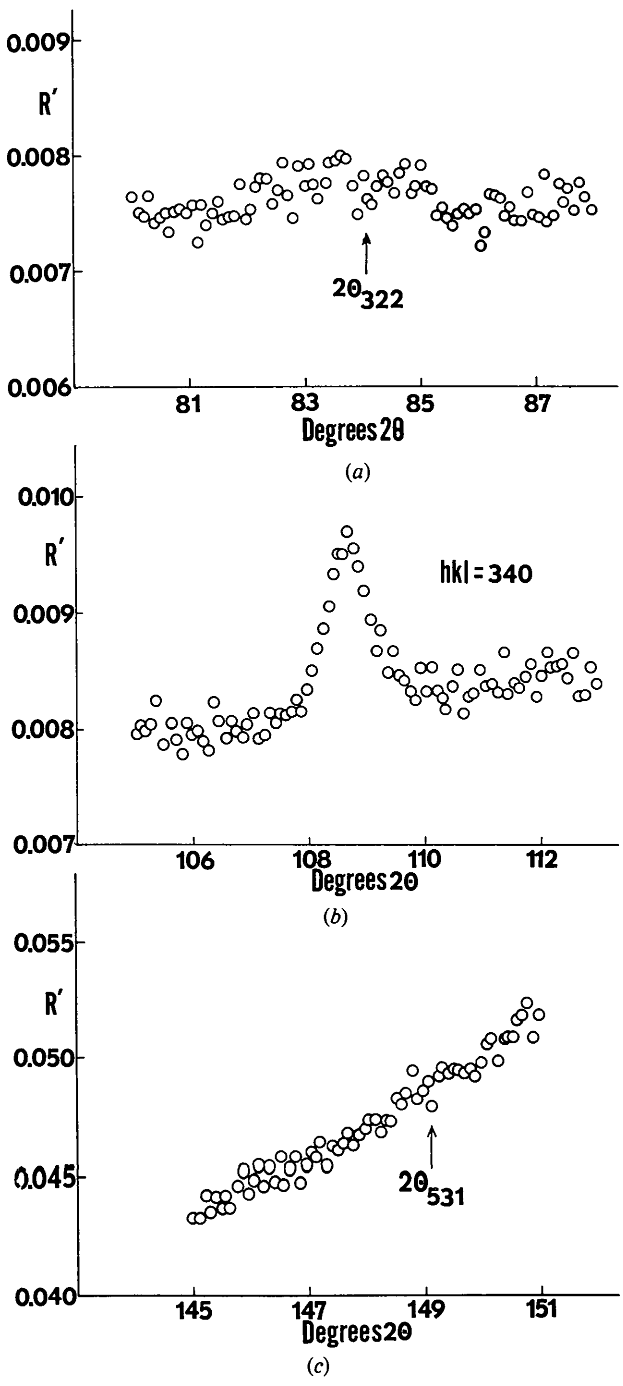

Fig. 1. Plots of R' *versus* 2θ for (*a*) hkl = 322, (*b*) hkl = 340, and (*c*) hkl = 531. The 2θ scale is nominal. Arrows indicate positions of the strong double-diffraction maxima observed upon rotation of the specimen about the diffraction vector.

2θ positions indicated in Fig. 1 are those of strong double-diffraction maxima observed as the specimen was rotated about the diffraction vector.

It has been shown (Borie, 1974) that for $hkl = 140$ and 340, thermal excitation of these maxima may include contributions both from the nonspherical character of the thermal motion and from its anharmonicity. For 531, however, there may be a contribution only from anharmonicity. It is easy to show that a similar result obtains for contributions to the forbidden maxima from a static but nonspherical electron distribution: for 140 and 340 there may be contributions if the distributions are either nonspherical or noncentrosymmetric; for 531 only noncentrosymmetric distributions result in excitation of the maximum. Of course, for nonspherical electron density effects, the degree of excitation depends on the details of the Fourier transform of the actual electron density and therefore on the magnitude and direction of the diffraction vector for the relevant maximum. Except in the unlikely eventuality that the effects of anharmonicity and noncentrosymmetry just cancel each other at $hkl = 531$, the absence of this reflection suggests that for V_3Si at room temperature these effects must be very small.

From a statistical analysis of a large number of high-angle reflections (which should not be affected significantly by nonspherical valence-electron distributions), Staudenmann & Testardi (1979) have inferred two second moments (measures of anisotropy) and a third and fourth moment (measures of anharmonicity) for the thermal motion of vanadium in V_3Si. Their data show no evidence for anharmonicity in the motion of silicon in this compound. From their result at room temperature we have computed the structure factors to be expected for the three forbidden reflections whose measurement we report here. A sign error in the Staudenmann–Testardi parameter α_V (Staudenmann, 1980) has been accounted for in our calculation. Table 1 compares this calculation with our result. As a further check of the validity of our measurements the table also includes observed and calculated structure factors for the allowed reflections $hkl = 341$ and 530. These measurements were self-calibrated with the fluorescent radiation and double-diffraction contributions were avoided, as described above.

Table 1. *Observed and computed structure factors for* V_3Si

$h\,k\,l$	F_{hkl}(observed)	F_{hkl}(computed)
1 4 0	0·33	0·09
3 4 0	0·16	0·12
3 4 1	6·63	6·41
5 3 0	5·75	5·61
5 3 1	nil	0·07

Good agreement for the allowed reflections confirms our method for interpreting our data. For both $hkl = 140$ and 340 our measured values are large. Since these are relatively low-angle maxima, contributions to them from static nonspherical valence-electron distributions are quite possible. Agreement for the three forbidden maxima would be improved were the Staudenmann–Testardi third moment smaller (their analysis indicates considerable uncertainty for this parameter) and their anisotropy parameter α_V larger.

Our result indicates, we believe, that the observation of forbidden maxima is the most direct and accurate measure of thermal motion anomalies and valence-electron distributions for crystals with the A15 structure. A statistical analysis of allowed reflections depends on small changes in large numbers and is vulnerable to extinction effects difficult to account for. Double-diffraction effects are difficult to observe and avoid. Internal self-calibration of the measurements, provided the incident radiation excites signficant fluorescence in the sample, eliminates an unnecessary parameter in any effort to fit them with theory. Extension of these measurements further into reciprocal space so that more forbidden maxima are accessible, and their reproduction with neutrons so that static and dynamic contributions may be separated, should contribute insights into the electronic and thermal properties of A15's.

The author is indebted to C. J. Sparks Jr for help with the experiment, particularly the detector system, and for suggesting the internal calibration method. H. L. Yakel contributed calculations of the double-diffraction pattern to be expected. B. W. Batterman provided specimens of V_3Si used in this work.

References

BAMBYNEK, W., CRASEMANN, B., FINK, R. W., FREUND, H.-U., MARK, H., SWIFT, C. D., PRICE, R. E. & VENUGOPALA RAO, P. (1972). *Rev. Mod. Phys.* **44**, 716–813.

BILDERBACK, D. H. & COLELLA, R. (1975). *Phys. Rev. B*, **11**, 793–797.

BORIE, B. (1974). *Acta Cryst.* A**30**, 337–341.

BRAGG, W. H. (1921). *Proc. Phys. Soc. London*, **33**, 304–311.

COLELLA, R. & MERLINI, A. (1966). *Phys. Status Solidi*, **18**, 157–166.

FIELD, D. W. (1976). *Phys. Status Solidi A*, **36**, 597–601.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

MERISALO, M., JÄRVINEN, M. & KURITTU, J. (1978). *Phys. Scr.* **17**, 23–25.

ROBERTO, J. B. & BATTERMAN, B. W. (1970). *Phys. Rev. B*, **2**, 3220–3226.

STAUDENMANN, J.-L. (1980). Private communication.

STAUDENMANN, J.-L. & TESTARDI, L. R. (1979). *Phys. Rev. Lett.* **43**, 40–43.