$(a_0,a_1,-a_2,-a_3)$; $(a_0,-a_1,a_2,-a_3)$; (a_0,a_2,a_1,a_3); $(a_0,-a_2,-a_1,a_3)$; $(a_0,a_2,-a_1,-a_3)$; $(a_0,-a_2,a_1,-a_3)$. By using a stereographic projection it can be easily shown that one and only one of the eight above quaternions has a related rotation axis $[\alpha,\beta,\gamma]$ such that $\gamma \geq 0$ and $\alpha \geq \beta \geq 0$, the rotation angle θ being positive or negative. If the term a_0 of this latter quaternion hereafter supposed to be (a_0,a_1,a_2,a_3) is greater than all the terms of typical expressions (5.1) to (5.6), Table 2, it is deduced that this quaternion describes disorientation according to the definition of § 2. These latter conditions are expressed by the disorientation inequalities, Table 5. The sign + or − in these inequalities depends only on the sign of θ_d, positive or negative. When one inequality becomes strictly an equality, it defines the limits of $|\theta_d|$. $|\theta_d|$ maximal is found on the limits of domains I, II, III.

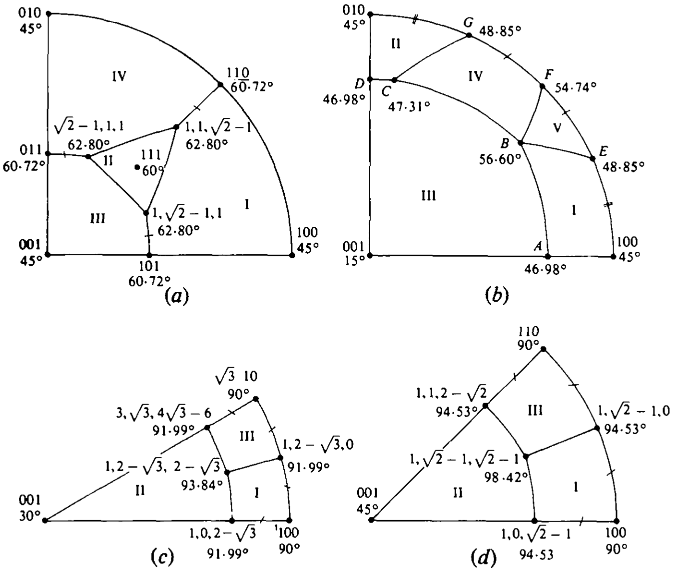

Fig. 4. Standard stereographic triangles with domains of maximum disorientation angles $|\theta_d|$. (a) cubic 1/cubic 2 [100, 110, 111], cubic/tetragonal: [100, $\bar{1}$10, 001], cubic/orthorhombic [100, 010, 001], (b) cubic/hexagonal, (c) hexagonal 1/hexagonal 2, (d) tetragonal 1/tetragonal 2. Equal angular spacings are slashed / or //.

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On the Space Group of Spinel, $MgAl_2O_4$

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Abstract

The controversial space-group problem of spinel, $MgAl_2O_4$, whether it is $Fd3m$ or $F\bar{4}3m$, was studied by electron diffraction. It was confirmed that the appearance of 'forbidden reflections' such as {200} was caused by the double reflection process of reflections with high indices on the non-zero-order Laue zone. Consequently, the space group of spinel is $Fd3m$, and the assignment of the space group to $F\bar{4}3m$ is ruled out.

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The change of space group from $F\bar{4}3m$ to $Fd3m$ associated with a phase transition, proposed by Mishra & Thomas [*Acta Cryst.* (1977), A**33**, 678], can also be explained by double diffraction: the magnitudes of primary reflections with high indices rapidly decrease due to the increase of the Debye–Waller factors at elevated temperatures.

Introduction

The space group of spinel, $MgAl_2O_4$, was first assigned as $O_h^7 = Fd3m$ in the work by Nishikawa (1915). The space group, however, has recently been thought to be either $Fd3m$ or $F\bar{4}3m$.

Hwang, Heuer & Mitchell (1973) claimed that the space group was $F\bar{4}3m$ on the basis of the interpretation of an electron diffraction pattern in which they found {200} reflections which are forbidden for the space group $Fd3m$. On the other hand, Samuelsen & Steinsvoll (1975) rejected the space group $F\bar{4}3m$ after observing the variation of the intensity of the 200 reflection with tilt around the scattering vector by neutron diffraction. As a result, they concluded that the peak 200 was due to a double reflection process. Thompson & Grimes (1977) performed an elaborate neutron diffraction experiment which showed substantial double diffraction. However, they made no decision on the space group, and suggested that electron diffraction had advantages for the observation of the forbidden reflections from spinel. This seems to be derived from the following discussion in Heuer & Mitchell (1975):

'As is well known (Hirsh, Howie, Nicholson, Pashley & Whelan, 1965), reflections of type $(h_1 + h_2, k_1 + k_2, l_1 + l_2)$ can arise from double diffraction when (h_1,k_1,l_1) and (h_2,k_2,l_2) are any two allowed primary reflections. As {220}, {400}, *etc.* are the only allowed reflections in the [001] zone-axis diffraction pattern, {200} reflections cannot arise from double diffraction.'

In addition to the discussion of the space group, which has not been settled yet, Mishra & Thomas (1977) proposed the presence of a second-order phase transition accompanied by the change of space group from $F\bar{4}3m$ to $Fd3m$. They believed that the {200} reflections, which appeared at temperatures below ~723 K and disappeared above that temperature, could be due to a low symmetry of the structure of spinel.

The preceding interpretation seems still unsatisfactory as a reason for the appearance of reflections which violate the presence of the *d*-glide plane in the structure of spinel. The possibilities of double diffraction must be considered not only with the reflections of type {*hk*0} but also with those of type {*hkl*} which are on the non-zero-order Laue zone. In order to examine the effect on double diffraction by reflections of the non-zero-order Laue zone, an electron diffraction experiment was performed in this investigation. As a result, the appearance of the alleged {200} reflections is concluded to be attributable to the double diffraction of reflections on the non-zero Laue zone in the symmetric [001] diffraction pattern.

In addition to the above investigation, it is discussed in this study why disappearance of the 'forbidden' reflection was observed by *in situ* electron diffraction experiments at elevated temperatures (Mishra & Thomas, 1977).

Experimental

The Ewald construction of [001] zone-axis electron diffraction is shown in Fig. 1. {1 21 1} reflections lie almost exactly on the reflecting sphere, provided that the accelerating voltage is 100 kV and the cell edge of spinel is 8·08 Å. This means that the 200 reflection can arise from the double reflection process of a pair of {1 21 1} reflections.

A number of electron diffraction patterns were taken, both by minutely tilting the electron beam around the [001] axis of a stoichiometric $MgAl_2O_4$ crystal and by operating at various accelerating voltages around 100 kV. The specimen was prepared

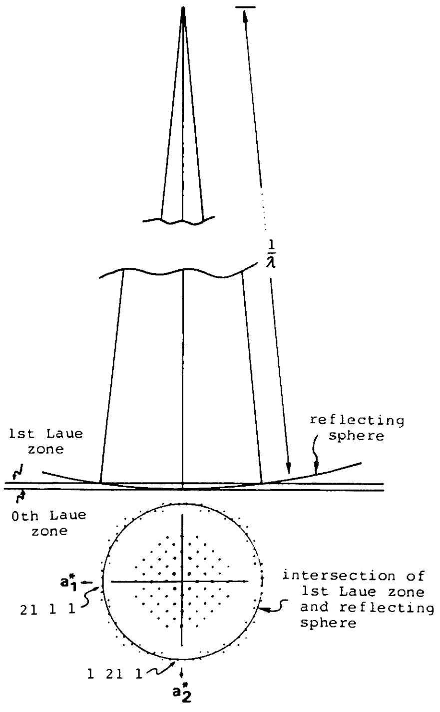
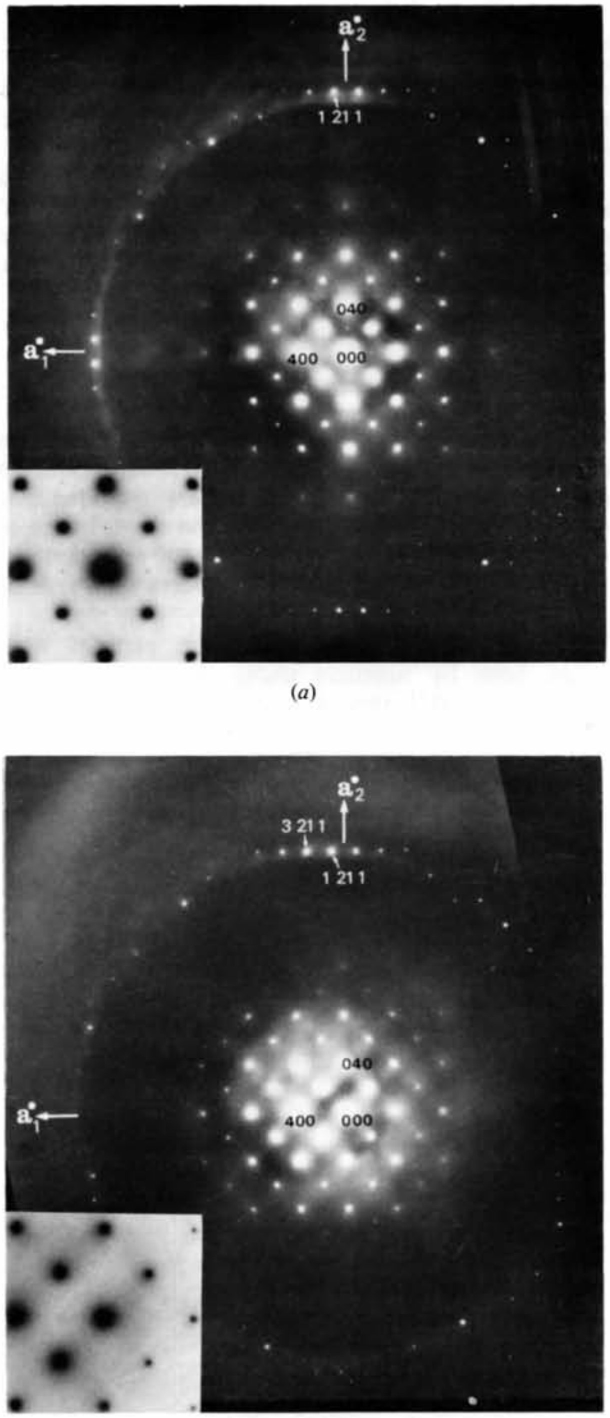


Fig. 1. The Ewald construction for electron diffraction. The direction of the incident beam is normal to (001). The radius of the reflecting sphere is 1/0·037 Å, and the interval between zero- and first-order Laue zones is 1/8·08 Å.



(a)

(b)

Fig. 2. The change of intensities of {200} due to tilting the incident beams. The central parts are enlarged and shown as inserts. (a) The incident beam is normal to (001). The intensities of the {200} reflections are symmetric around the origin. (b) The incident beam is tilted to excite the 400 reflection. The intensities of the {200} reflections are asymmetric around the origin. Only the 200 reflection of {200} is strong; the others are very weak or cannot be observed.

from the bulk crystal by ion thinning and examined in the Hitachi-12SE transmission electron microscope.

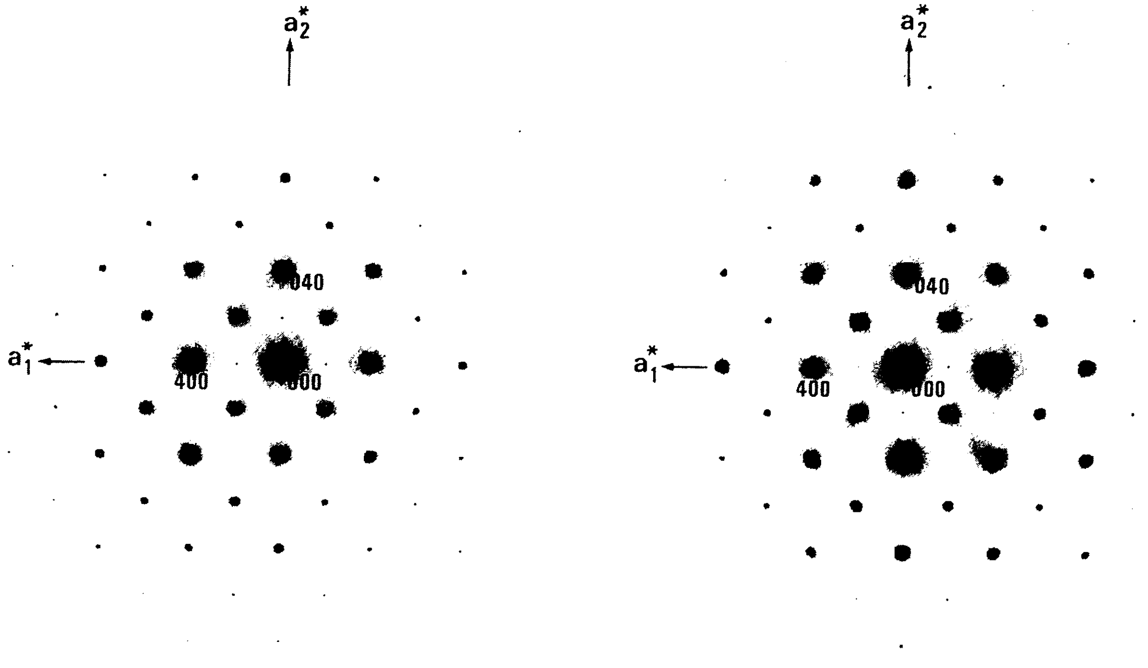
The examples of diffraction patterns obtained by tilting the beam are given in Fig. 2(*a*) and (*b*). The maximum value of $\sin\theta/\lambda$ is about 1·4 Å^{-1} in the observed range of the pattern. The reflections of the first Laue zone are clearly seen in the outer parts in addition to those of the zero-order Laue zone. The {200} reflections always appear in the central part together with {1 21 1} and/or {3 21 1} reflections which are on the first Laue zone. The intensities of {200} reflections are almost symmetric in Fig. 2(*a*), and they appear together with strong {1 21 1} reflections. However, only 200 of the {200} reflections is strongly observed and $\bar{2}00$, 020 and $0\bar{2}0$ are very weak or cannot be observed in Fig. 2(*b*). Fig. 2(*b*) was obtained under a slightly tilted condition so that the 400 reflection was intensely excited. In this case the 200 reflection appears together not only with 1 21 1 but also with strong 3 21 1 reflections. Other examples are shown in Fig. 3(*a*) and (*b*) which were obtained in order to examine the effect of the change in lattice constants on the diffraction patterns. The experiments were in fact performed by varying the accelerating voltage which gives the same effect as changing the lattice constants. Fig. 3(*a*) was produced under the same conditions as Fig. 2(*a*) but the accelerating voltage was increased by 0·9% in Fig. 3(*b*). No significant difference is observed between Fig. 3(*a*) and (*b*).

Discussion and conclusion

The {200} reflections are always observed together with {1 21 1} and/or {3 21 1} reflections on the first Laue zone. These experimental observations and the Ewald construction shown in Fig. 1 mean that {200} reflections arise from a double reflection process by a pair of {1 21 1} reflections such as 1 21 1 and $1\,\overline{21}\,\bar{1}$, or from that by 3 21 1 and $\bar{1}\,\overline{21}\,\bar{1}$ reflections. Furthermore, since the intensity of the 200 reflection drastically decreases or disappears with a minute change of the orientation of the incident beam upon the specimen, as shown in Fig. 2(*a*) and (*b*), it is concluded that the structure factor of 200 does not have a finite value but is in fact zero.

It is interesting to discuss the phenomenon of the appearance and disappearance of the 'forbidden' reflections which was observed by electron diffraction at high temperatures (Mishra & Thomas, 1977). The appearance is of course attributed to a double diffraction process as shown in the experiments and the preceding discussions. The disappearance may be ascribed to a slight change in the diffraction conditions with at least three possibilities: (1) a slight change of lattice constants through a change of temperature, (2) a change of specimen orientation in the two experiments at temperatures above and below 723 K, and (3) the change of the Debye–Waller factor with temperature. The probability of the first case is quite low because the experiments with increasing accelerating voltage, which apparently gives the same effect as expanding the lattice, did not give the drastic decrease of the intensities of {200} reflections as shown in Fig. 3(*a*) and (*b*). The second does not seem possible either because the experiments at elevated temperatures by Mishra & Thomas (1977) were made by keeping the orientation of the specimen at the position where the 400 reflection was always strongly excited. The third possibility is most likely in this case. Since the Debye–Waller factor for the reflection with high indices is sensitive to the temperature change, structure factors of {1 21 1} and {3 21 1} reflections will rapidly decrease with increasing temperature. The reason why the steady decrease of the structure factor causes rather abrupt disappearance of 'forbidden' reflections can be discussed as follows. According to the dynamical theory of electron diffraction, a Bragg reflection takes place effectively only when the geometrical relation between the incident beam and the crystal is confined to a narrow range around the exact Bragg angle. If the two-beam approximation is valid, the narrow range is proportional to the structure factor. Even in the many-beam case, this range seems to be largely unaffected by the presence of the other beams. The experimental conditions given by Mishra & Thomas (1977), which allow a small deviation from the exact Bragg condition for both 'forbidden' 200 and 'primary' 1 21 1 or 3 21 1 reflections, allow for the spinel at lower temperatures to produce double diffraction. That is to say, the structure factors of 'primary' 1 21 1 and 3 21 1 are large enough to excite the 200 beam at lower temperatures. When the structure factors of 'primary' reflections become smaller than a critical value, the same geometrical condition causes a larger deviation from the diffraction condition. Therefore, the effective double diffraction by the reflection on the non-zero Laue zone can no longer take place at elevated temperatures.

In conclusion, the appearance of forbidden reflections such as {200}, {420}, *etc.* for space group *Fd*3*m* of spinel is attributed only to the double-diffraction process of the strong reflections on the non-zero Laue



(*a*) (*b*)

Fig. 3. Comparison of diffraction patterns with different accelerating voltages. (*a*) The same condition as Fig. 2(*a*), approximately 100 kV. (*b*) The accelerating voltage is 0·9% higher than (*a*).

zone, and this result rules out the possibility of the space group being $F\bar{4}3m$ rather than $Fd3m$.

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Analysis of Multiple Inelastic Scattering of Electrons Incident on Crystalline Specimens

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Abstract

An approximate expression is given for describing Bloch-wave amplitudes of electrons which undergo multiple inelastic scattering in crystalline specimens. The expression is derived from differential equations of inelastic scattering given by Howie [*Proc. R. Soc. London Ser. A* (1963), **271**, 268–287]. In the course of the derivation, the differential equations are reduced to a transport equation which has been applied to the analysis of multiple inelastic scattering in non-crystalline specimens. The identity between them is discussed, including the approximations employed. The expression was used to analyze Bloch-wave amplitudes of transmitted electrons at various thicknesses of copper and silicon crystals. It was found that the values of the amplitudes were sensitive to the shape of the interaction potential resulting from the excitation of core electrons. An accurate estimate of the potential will be required in future studies.

1. Introduction

The intensity of electrons passed through thin crystals shows a diffuse distribution around each diffraction spot and the distribution is normally anisotropic (*e.g.* Kikuchi patterns). This is due to the dynamical diffraction effect of inelastically scattered electrons. The theoretical study on the diffuse intensity was first made by Kainuma (1955) and subsequently by Takagi (1958*a*,*b*). Since then a number of theoretical studies have been made (Fujimoto & Kainuma, 1963; Okamoto, Ichinokawa & Ohtsuki, 1971). These theories succeeded in interpretating qualitative features of both Kikuchi lines and bands. It is well known, however, that the quantitative prediction is still unsatisfactory for thick specimens since the analysis is made within the framework of single inelastic scattering. Meanwhile, there is an increasing interest in analyzing diffraction patterns of bulk specimens which are obtained with reflective high-energy electrons and back-scattered electrons. In these cases, the effect of multiple inelastic scattering is so prominent that the knowledge as regards the behavior of diffusely scattered electrons is required in more detail.

Recently, several theoretical approaches to the analysis of multiple inelastic scattering have been proposed (Kamiya & Shimizu, 1976; Rez, 1978). In a previous report (Yamamoto, Mori & Ishida, 1978), the authors also attempted to deal with multiple inelastic scattering using a Monte Carlo method and studied the contrast of electron channelling patterns in scanning electron microscopy. In this approach, however, the

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