DETERMINATION OF THE V4-CENTER STRUCTURE IN KBr CRYSTAL BY MEANS OF DOUBLE ALIGNMENT CHANNELING TECHNIQUE

Y. Mitsushima, K. Morita, N. Matsunami, N. Itoh

► To cite this version:

Y. Mitsushima, K. Morita, N. Matsunami, N. Itoh. DETERMINATION OF THE V4-CENTER STRUCTURE IN KBr CRYSTAL BY MEANS OF DOUBLE ALIGNMENT CHANNELING TECHNIQUE. Journal de Physique Colloques, 1976, 37 (C7), pp.C7-95-C7-100. 10.1051/jphyscol:1976714 . jpa-00216864

HAL Id: jpa-00216864

<https://hal.science/jpa-00216864>

Submitted on 1 Jan 1976

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

DETERMINATION OF THE V_4 -CENTER STRUCTURE IN KBr CRYSTAL BY MEANS OF DOUBLE ALIGNMENT CHANNELING TECHNIQUE

Y. MITSUSHIMA, K. MORITA, N. MATSUNAMI and N. ITOH

Department of Nuclear Engineering, Nagoya University, Nagoya, Japan

Résumé. — Nous avons déterminé la position des atomes interstitiels impliqués dans les centres V_4 de cristaux de KBr par la technique de channeling par alignement double. Une mesure d'absorption optique d'un cristal de KBr irradié par des protons ou des atomes d'hélium à la température de l'azote liquide nous a assurés que la courbe V_4 est un défaut interstitiel principalement produit par le rayonnement. Un faisceau bien collimaté d'ions He^+ , de 1,25 MeV, a été envoyé parallèlement à la direction $[110]$ des cristaux de KBr. La dépendance angulaire de la production d'ions hélium renvoyés dans le plan $[100]$ autour de la direction $[\bar{1}00]$ et de la direction $[\bar{1}10]$ ont été mesurées à la température de l'azote liquide et possèdent respectivement un pic large au centre et un pic double. La méthode de Monte Carlo a été employée pour calculer la dépendance angulaire de la production d'atomes renvoyés pour différentes positions interstitielles dans le channeling en double alignement. La comparaison entre les résultats expérimentaux et calculés indique qu'un atome de Br interstitiel du centre V_4 occupe une position proche du centre du corps. Des expériences d'optique et de channeling, nous avons conclu que le centre V_4 est une molécule neutre d'halogène dont chaque atome est situé dans la position décrite ci-dessus.

Abstract. — The position of interstitial atoms involved in the V_4 -center in KBr crystal has been determined with the double alignment channeling technique. An optical absorption measurement of KBr crystal irradiated with protons or heliums at liquid nitrogen temperature assured that the V_4 -center is the predominant radiation-induced interstitial defect. A well collimated beam of 1.25 MeV He^+ ions was incident parallel to the $[110]$ direction of KBr crystals. Angular dependence of the yield of the backscattered helium ions in the (100) plane around the $[\bar{1}00]$ direction and the $[\bar{1}10]$ direction was measured at liquid nitrogen temperature and found to have a broad peak at the center and a double peak, respectively. The Monte Carlo method was employed to calculate the angular dependence of the backscattering yield for several interstitial positions in the double alignment channeling. Comparison between the experimental and calculated results indicates that an interstitial Br atom of the V_4 -center occupies a position near the body center. From the optical and channeling experiments, it was concluded that the V_4 -center is a neutral halogen molecule, each atom of which is located at the position described above.

1. Introduction. — It is well known that X-ray irradiation or electron irradiation of alkali halides produces halogen Frenkel pairs [1]. At liquid helium temperature an F-center and an H-center constitute a Frenkel pair. The F-center is an electron trapped by a halogen ion vacancy and the H-center is an interstitial neutral halogen atom which forms an X_2^- molecule at an anion site [2]. The H-centers are unstable at liquid nitrogen temperature, where a V_4 -center is the complementary pair of the F-center [3]. The V_4 -center is known to comprise two interstitial neutral halogen atoms and to have a molecular symmetry axis along a $\langle 100 \rangle$ direction. Its structure, however, has not been definitely established yet. The EPR technique, which has been frequently used to study color centers, cannot be applied to determine its structure owing to its diamagnetic nature.

Theoretical works on the di-interstitial centers in alkali halides have been made by several authors.

White *et al.* [4] have calculated the energy required to place a Cl_2 molecule in a NaCl lattice, each Cl atom being situated in the proximity of the body center of the small cube (one eighth of the unit cell). On the other hand, Catlow *et al.* [5] compared the energy of various configurations of the di-interstitials in NaCl and found that the Cl_3^- molecule at an anion site with a $\langle 111 \rangle$ orientation is more stable than the interstitial Cl_2 molecule described above.

The channeling technique has been applied to determine the location of the interstitials in crystal lattices [6, 7]. Single alignment channeling technique has been widely used to determine the impurity location: the incident beam is scanned around a major crystal axis and the particles scattered into a random direction are counted. This technique cannot be used to locate the self-interstitial atoms since the particles scattered by the regular lattice atoms are usually more numerous than those scattered by the interstitial

atoms. Double alignment channeling technique [8-10], in which both the incident and outgoing beams are aligned simultaneously to major axes, reduces the yield from the regular lattice atoms to $\sim 0.1\%$ of the random yield. Therefore, in double alignment channeling experiments the scattering yield from interstitials at a concentration of 10^{-3} is comparable with that from regular lattice atoms. Appleton *et al.* [8] made investigations of interstitial Zn concentration in additively colored ZnO. Morita *et al.* [10] measured the dependence of the intensity of the backscattered particles (yield profile) into a planar channel on the angle of deviation from a certain crystal axis of irradiated silicon crystals. They also calculated [11] the yield profile for the silicon atom located at various positions in the Si-lattice with the Monte Carlo computer simulation. From the comparison between the experimental and calculated yield profiles, the location of the interstitial silicon atoms has been determined.

The purpose of the present paper is to determine the location of the interstitial halogen atoms in the V_4 -center by means of the double alignment channeling technique. The optical absorption of KBr crystals irradiated with H^+ , H_2^+ or He^+ ions was measured at liquid nitrogen temperature and it is confirmed that the interstitial defect produced predominantly is the V_4 -center. The backscattering yield profiles in double alignment were measured and compared with the yield profiles for various interstitial sites calculated with the Monte Carlo method. The location of the atoms of the V_4 -center was determined.

2. Experimental procedure.— Pure KBr crystals, which were obtained from the Harshaw Chemical Company, were cleaved just before irradiation and mounted on a copper disc which was firmly held on a goniometer placed in a target chamber. The goniometer assembly can be rotated around the vertical (tilt angle) and horizontal (azimuthal angle) axes. The specimens were irradiated with H^+ , H_2^+ or He^+ beams, which were generated from a Van de Graaff accelerator at Nagoya University. The irradiation and measurements were made at liquid nitrogen temperature. The pressure of the target chamber was about 3×10^{-6} torr.

After bombardment of 1.5 MeV H_2^+ or He^+ particles on a specimen with a beam current of around 60 nA/cm², the optical absorption was measured with a conventional technique. The dichroism of the V_4 -center was determined in the following way. After bombardment the specimens were bleached with U. V. radiation polarized along the [001] axis or [011] axis and the absorption was measured with radiation polarized parallel and perpendicular to the bleaching radiation. The bleaching light was obtained from a mercury lamp through a UV-D25 filter (Toshiba).

The He^+ beams of 1.25 MeV were collimated to an

angular spread less than 1.3×10^{-3} rad by two slits of 2 mm and 0.3 mm in diameter. The backscattered He ions were detected with plastic films (Cellulose Nitrate of $\sim 15 \mu\text{m}$ in thickness) placed at the direction of the $[100]$ and $[\bar{1}10]$ axes. This technique has an advantage that the fluctuation of the incident beam current during the measurement does not affect the obtained yield profile. The distances from the crystal to the detector placed at the $[100]$ and the $[\bar{1}10]$ directions were 12 cm and 20 cm, respectively.

After the exposure, the film was etched for 10 ~ 20 minutes in 6N NaOH maintained at $\sim 60^\circ\text{C}$. The particle tracks on the etched film were counted with a conventional light microscope combined with the automatic television counter. The spatial distributions of particle tracks on the film were obtained from the counts in the area of $0.1 \times 0.13 \text{ mm}^2$ and of $0.2 \times 0.26 \text{ mm}^2$ for the $[100]$ and $[\bar{1}10]$ axes, respectively. From the obtained spatial distributions of the particle tracks, the dependence of the scattering yield on the tilting angle in the (100) plane from both axes were deduced.

The optimum number of the tracks on the films is $\sim 10^4 \text{ mm}^{-2}$. To monitor the number of the particles being bombarded on the film, a Si-surface-barrier detector with a sensitive area of 25 mm^2 and apart from the target crystal by 7 cm was used. The discrimination level of the counting system was set at the threshold energy, 400 keV, of the plastic film for detecting He^+ ions. The bombardment was continued until the number of the tracks on the films reaches the optimum value. The beam current was $1.5 \mu\text{A/cm}^2$.

3. Experimental results.— The change in the optical absorption spectrum of KBr crystal by irradiation with H_2^+ at a dose of $5 \times 10^{13} \text{ cm}^{-2}$ is shown by the solid line in figure 1. The broken line is the optical absorption spectrum of KBr crystal irradiated with X-rays at liquid nitrogen temperature. The two

FIG. 1. — Optical absorption spectra of KBr irradiated with 1.5 MeV H_2^+ beams (solid line) and X-rays (broken line) at liquid nitrogen temperature. Two curves were normalized at the peak height of the F band.

curves were normalized at the peak height of the F band. The comparison between two spectra shows that the peak heights of the V_4 -band agree each other, although in the case of the H_2^+ irradiation background in the high energy side of the V_4 -band is raised. This shift of the background may be ascribed to the surface defects due to sputtering by the H_2^+ bombardment. The average concentration of the F-center over the range 14.1 μm of 750 keV H^+ was evaluated to be 1.5×10^{-3} with the value 0.8 of the oscillator strength of the F-center. Essentially the same absorption spectra were obtained by He^+ irradiation.

The specimens irradiated with He^+ ions at a dose of $8 \times 10^{12} \text{ cm}^{-2}$ were bleached with light polarized along [001] and [011]. The difference in the concentrations of the V_4 -center oriented parallel and perpendicular to the bleaching light was measured as a function of bleaching time. The difference divided by the initial concentration of the V_4 -center is plotted in figure 2. It is seen that the dichroism is produced only by the [001] bleaching, indicating that the symmetry axis of the V_4 -center is $\langle 100 \rangle$. These results agree with the symmetry property of the V_4 -center produced by X-ray irradiation [12].

FIG. 2. — Dependence of the degree of polarization in the absorption coefficients of the V_4 -band incident along [100] and polarized along [001] (O) and along [011] (□).

The backscattering yield profiles around the [100] and $\bar{1}10$ directions of irradiated KBr are shown in figure 3. The abscissa is the tilting angle or the detector angle within the $\{\bar{1}10\}$ -plane. The tilting angle is the angle between the axial direction and the direction of the outgoing beam reaching at a given detector position. The detector angle is divided by the half-angle $\psi_{1/2}$, which was calculated with Andersen's procedure [13] to be 0.011 rad and 0.009 rad for the [100] and $\bar{1}10$ directions, respectively. The yield profile around the [100] direction shows a broad peak at the center and around the $\bar{1}10$ direction shows a small double peak at $\psi/\psi_{1/2} = 0.3$. These results show that the interstitial atoms occupy the mid-chan-

FIG. 3. — Experimental backscattering yield profile in a (100) tilt plane of the helium ions from a radiation damaged KBr crystal at liquid nitrogen temperature. The direction of incidence is [110] and the abscissa is the angle between the outgoing direction and the $\bar{1}10$ axis (a) and $\bar{1}10$ axis (b), divided by the half angle $\psi_{1/2}$ of the $\langle 100 \rangle$ axis. Incident energy is 1.25 MeV and the width marked by arrows in the figure shows the angular resolution.

nel position in a $\langle 100 \rangle$ channel and do not occupy the mid-channel position in a $\langle 110 \rangle$ channel.

4. Discussions. — **4.1 CALCULATION OF BACKSCATTERING YIELD PROFILE.** — From the single alignment, the backscattering yield from an atom at a given lattice position is known to be equal to the average flux density of channeled particles with a weight of the probability density of thermal vibration. The probability that a scattered atom emerges out from the crystal is also given by a similar average flux density in the outgoing channel. Therefore the scattering yield for the double alignment may be calculated by multiplying the average flux densities at the defect position in the incoming and outgoing channels.

The channeled particles distributions at a depth of 1000 layers in a KBr lattice at 77 K were calculated with the Monte Carlo method for 1.25 MeV He^+ ions incident in an angular range of 0 to 0.022 rad around a $\langle 100 \rangle$ axis and 0 to 0.018 rad around a $\langle 110 \rangle$ axis, the plane of incidence always being a (100) plane. The method of calculation used here was the same as that presented by Morita [11]. With the flux distributions obtained from the calculations, the

relative double alignment backscattering yield by Br atoms placed on the regular lattice position, the face-centered interstitial position and the body-centered interstitial position were calculated. The incident direction was a $\langle 110 \rangle$ axis and the outgoing directions were $\langle 110 \rangle$ and $\langle 100 \rangle$ axes. Figure 4 shows the results from the face-centered atoms and the body-centered atoms for the outgoing direction of $\langle 100 \rangle$ and $\langle 110 \rangle$. In this figure $\psi/\psi_{1/2} = 0$ represents a $\langle 110 \rangle$ axial direction, whereas the plateau at $\psi/\psi_{1/2} > 1.5$ represents the scattering into the (100) plane. The relative backscattering yield profiles from the regular lattice atoms show monotonous dips.

FIG. 4. — Angular dependence of the calculated relative scattering yield of helium ions backscattered from body-centered atoms (dashed line) and face-centered atoms (solid line) in the double alignment channeling. The incident channeling direction is $\langle 110 \rangle$ and outgoing direction is tilt in the (100) plane from the $\langle 100 \rangle$ axis (a) and the $\langle 110 \rangle$ axis (b).

The relative scattering yield R from a crystal containing defects may be calculated by superposition of the yield R_i from the interstitial atoms on the yield R_L from the atoms in the regular lattice sites ;

$$R = cR_i + R_L, \quad (1)$$

where c is the fractional concentration of the interstitial atoms.

4.2 DISCUSSION OF THE EXPERIMENTAL RESULTS. —

From the optical experiments, it was confirmed that the irradiation of KBr crystals with H^+ and He^+

at liquid nitrogen temperature produces the F-center and the V_4 -center and that the produced V_4 -center has a $\langle 100 \rangle$ symmetry axis. Since the ratio of the height of the V_4 -band to that of the F-band is the same for charged particles and X-rays irradiation, one may conclude that no other interstitials than the V_4 -center are produced by particle irradiation. The distortion of the lattice by the F-center may be so small [14] that the channeled particles will not be scattered. Therefore the backscattering yield profiles around the major axes may reflect the location of the interstitial atoms of the V_4 -center. In view of the calculated results, the existence of the peak at the $[100]$ direction and its absence at the $[110]$ direction in the experimental yield profiles lead to a conclusion that the interstitials of the V_4 -center are located near the body center. As seen from figure 3, a double-peak is observed at $\psi/\psi_{1/2} = 0.3$ for the outgoing direction of $[110]$. A similar peak is also seen at $\psi/\psi_{1/2} = 0.3$ in the calculated result for the body-centered position. Calculations were also made for several interstitial positions and it turns out that the peak disappears when the interstitial is deviated by a $1/8$ of the lattice constant from the body center. The deviation of the interstitial position by $1/12$ of the lattice constant from the body center does not affect the yield profile appreciably. Thus it is concluded that the position of the interstitial halogen of the V_4 -center is within a $1/8$ of the lattice constant from the body-centered position.

It has been shown [15] that the production of the Frenkel defects is saturated at a concentration of around 5×10^{-3} . The relative yield profile of the $\langle 100 \rangle$ outgoing direction for KBr crystal including body-centered interstitials at a fractional concentrations of 5×10^{-3} were calculated according to eq. (1). The calculated yield profile and the experimental profile are shown in figure 5, where the values of the yield are normalized by the height of the peak. The calculated yield profile (a) shows a rapid rise towards the planar direction. It is seen in figure 5 that the experimental yield at the planar direction is smaller than the calculated yield by a factor of 2.5. This discrepancy may be caused by the fact that the ratio of the scattering yield from the regular lattice atom for $\psi/\psi_{1/2} = 0$ to that for $\psi/\psi_{1/2} = 2.0$ is overestimated.

In the present experiment, as described previously, the He^+ ions backscattered between the maximum penetration depth of $1 \mu m$ and the crystal surface were counted. On the other hand the computer simulation was carried out to the maximum depth of about $0.3 \mu m$. As well known, the dechanneling caused by atomic electrons and thermally vibrating atoms increases the backscattering yield of He^+ ions at large penetration depth. Moreover, the interstitial defects and also the alkali and halogen ions displaced due to the presence of the interstitial ion make a considerable contribution on dechanneling [16]-[18].

FIG. 5. — Angular dependence around the $\langle 100 \rangle$ axis and in the (100) plane of the calculated relative scattering yield of helium ions backscattered from a KBr crystal containing body-center interstitials at a fractional concentration 5×10^{-3} (curve (a)). Experimental angular dependence around $\langle 100 \rangle$ axis and in the (100) plane is represented by curve (b). Each yield profile is normalized by the value of the yield at $\psi/\psi_{1/2} = 0$.

The dechanneling may reduce the relative scattering yield from the lattice ions at the planar direction more predominantly than that at the channeled direction, as described below. In a perfect channel, the yield ratio at the axial direction to the planar direction may be the ratio of the emission yields of particles from thermally vibrating atoms into the axial and planar direction. This ratio has been used to obtain the curve (a) of figure 5. Due to the dechanneling effect only $(1-\bar{\chi}_a)$ of the particles emitted into an axial channel can reach the surface, where $\bar{\chi}_a$ is the average minimum yield over the distance of $0 \sim 1 \mu\text{m}$ for the axial channel. Similarly for the planar channel, the emission yield is reduced by a factor of $(1-\bar{\chi}_p)$, where $\bar{\chi}_p$ is the average yield for the planar channel. It follows that the dip for the yield profile shown curve (a) in figure 5 is reduced by a factor of $(1-\bar{\chi}_a)/(1-\bar{\chi}_p)$ due to the dechanneling. $\bar{\chi}_a$ and $\bar{\chi}_p$ were obtained by a backscattering experiment to be $\bar{\chi}_a = 0.30$, $\bar{\chi}_p = 0.66$. Thus the dip in the calculated yield profile in figure 5 should become shallower by a factor of 2. This factor is an underestimate, since the channeled particle emitted from an atom near a lattice position possesses high

transverse energy, whereas $\bar{\chi}_a$ and $\bar{\chi}_p$ were obtained with a collimated beam.

The other effect which has not been taken into account is the effect of backscattering from the displaced atoms around the interstitial. According to Diller's calculation the distortion of the neighboring ions is as large as 15 % and is nearly along $\langle 111 \rangle$ axes for most of the neighboring ions [19]. The incident channeled particles scattered by these distorted atoms produce a yield profile with smaller dip than those scattered by lattice ions. The yield profile caused by the distorted ions should be added to that caused by thermally vibrating atoms shown in figure 5. According to the work by Miyagawa *et al.* introducing a few per cent of substitutional Br in KCl causes a increase of the axial minimum yield by three times of the theoretical minimum yield [20]. In view of the fact that the distortion around the interstitial defects is much larger than that around the substitutional Br, it appears that the distorted lattice around the interstitial Br molecule of 0.5 % in concentration may flatten considerably the yield profile curve which is obtained for an undistorted lattice.

The half width of the peak of the experimental yield profile around the $[100]$ axis is nearly twice of that of the calculated yield profile for the body-centered position. This discrepancy may be partly ascribed to that Br atom does not situate exactly at the body-centered position described above. The other cause of the broadening of the peak may be the dechanneling effect.

The location of the interstitials constituting the V_4 -center to be near the body-centered position may satisfy both the White's model and Catlow's model. According to the dichroic bleaching measurement, however, the V_4 -center in KBr is known to be oriented along a $\langle 100 \rangle$ direction [21]. In view of the $\langle 100 \rangle$ symmetry of the V_4 -center, the present investigation supports the White's model of the V_4 -center shown in figure 6, although a good agreement

FIG. 6. — A model of the V_4 -center in KBr lattice.

has been obtained between theoretical energies of X_3^- and of V_4 -center in KCl, KBr and KI ⁽¹⁾. It is also possible that the model of the V_4 -center may not be so simple as proposed by White and coworker. The Cl_2 molecule may form a molecular bonding with the neighboring Cl^- ions which are on the crystal plane

(1) Tasker, P. W., private communication.

intersecting with the molecular axis. According to the White's calculation the distance between Cl atoms in Cl_2 is 1.974 Å. This value is smaller than the half of the lattice constant and may explain the broadening of the peak.

Authors are grateful to the member of the Van de Graaff group cooperation. They also express their gratitude to A. M. Stoneham and P. W. Tasker for the valuable discussions concerning to the model of the V_4 -center.

References

- [1] SONDER, E. and SIBLEY, W. A., *Point Defects in Solids* ed. J. H. Crawford, Jr. and L. M. Slifkin (Plenum, New York) (1972) 201.
- [2] FOWLER, W. B., *The Physics of Color Centers*, ed. W. B. Fowler (Academic Press, New York) 1968 p. 53 and KABLER, M. N., *Point Defects in Solids*, ed. J. H. Crawford, Jr. and L. M. Slifkin (Plenum, New York) 1 (1972) 327.
- [3] ITOH, N., *Cryst. Lattice Defects* 3 (1972) 115.
- [4] WHITE, W. W. and GREENE, A. C., *Cryst. Lattice Defects* 1 (1970) 83.
- [5] CATLOW, C. R. A., DILLER, K. M. and NORGETT, M. J., *J. Phys. C* 8 (1975) 134.
- [6] GEMMELL, D. S., *Rev. Mod. Phys.* 46 (1974) 129.
- [7] MORGAN, D. V. (ed), *Channeling* (John Wiley, New York) 1973.
- [8] FELDMAN, L. C. and APPLETON, B. R., *Appl. Phys. Lett.* 15 (1969) 305 ;
APPLETON, B. R. and FELDMAN, L. C., *Atomic Collisions in Solids*, ed. D. W. PALMERS, M. W. Thompson and P. D. Townsend (North Holland, Amsterdam) 1970, p. 417.
- [9] PICRAUX, S. T., BROWN, W. L. and GIBSON, W. M., *Phys. Rev. B* 6 (1972) 1382.
- [10] MORITA, K. and CARSTANJEN, H. D., *Rad. Effects* 28 (1976) 97.
- [11] MORITA, K., *Rad. Effects* 28 (1976) 65.
- [12] KINGSLEY, J. D., *J. Phys. & Chem. Solids* 23 (1962) 949.
- [13] ANDERSEN, J. U. and FELDMAN, L. C., *Phys. Rev. B* 1 (1970) 2063.
- [14] STONEHAM, A. M., *Theory of Defects in Solids* (Oxford University Press, London) 1975.
- [15] POOLEY, D., *Brit. J. Appl. Phys.* 17 (1966) 855.
- [16] BEHRISH, R., *Ion Beam Surface Layer Analysis*, ed. O. Meyer, G. Linker and F. Käppler (Plenum Press New York) 1975.
- [17] MATSUNAMI, N. and ITOH, N., *Phys. Lett.* 43A (1975) 435.
- [18] MATSUNAMI, N., *J. Phys. Soc. Japan* 38 (1975) 848.
- [19] DILLER, K. M., Thesis (1975).
- [20] MIYAGAWA, S., MORITA, K., MATSUNAMI, N., TACHIBANA, K., and ITOH, N., *Rad. Effects* 13 (1972) 271 and unpublished results.
- [21] ITOH, N., *J. Phys. & Chem. Solids* 27 (1966) 197.

DISCUSSION

C. JACCARD. — Do you take *flux peaking* into account in the calculation of the yield *vs* angle ?

N. ITOH. — Yes. In the Monte Carlo calculation, the flux peaking is automatically taken into account. It is indeed due to the flux peaking that the location could be made.