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Ion channeling in natural diamond. Minimum yields

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Reasons for the desirability of obtaining a comprehensive set of good ion-channeling measurements for diamond are outlined. Good-quality crystals must first be selected from the available natural specimens, and experiments are reported which show that the best selection criterion is the channeled minimum yield itself. Methods of improving the crystal quality and precautions to be taken to ensure accurate results are considered. Minimum-yield measurements were made for a variety of axes, planes, ions, energies, and diamond temperatures. The results agree quite well with theoretical predictions. The very small value of the thermal vibration amplitude in diamond even at moderately elevated temperatures (relative to the Thomas-Fermi screening distance) provides a good test of theory and enables the values of certain parameters to be determined with greater accuracy than is usually possible. The inadequacy of a simple geometrical model for the origin of the minimum yield is emphasized by its predominant dependence on thermal vibrations even in this very "cold" crystal. These experiments also shed some light on the nature of the free diamond surface.

I. INTRODUCTION

Ion channeling has now been demonstrated in single crystals of a great variety of substances.[1] An understanding of the physics of the phenomenon, together with theoretical estimates of the critical angles for axial and planar channeling, and of the minimum yields of nuclear-encounter processes initiated by channeled ions, have been given in the work of Lindhard,[2,3] Andersen,[4,5] and others.[6,7] Although these workers were able to predict the correct functional dependence of the above quantities on most of the parameters involved, their quantitative predictions were not exact. It fell to Barrett[8] to produce semiempirical expressions, rooted in the continuum model of Lindhard and others but fitted by computer simulation techniques, which have been shown to predict the measured values of critical angles and minimum yields quite accurately in a large number of different crystals at various temperatures and ion energies.

Most channeling work has been carried out on silicon, and a large amount also on germanium, both elements in group IV of the periodic table, crystallizing in the fcc variant known as the diamond structure. It is obviously of interest to perform comparative experiments on a third such crystal, namely, diamond itself. But there is an even greater interest in diamond from the channeling point of view. The theoretical expressions due to Barrett all contain the two parameters u_1 (the rms thermal vibration amplitude in one dimension) and a (the Thomas-Fermi screening distance of the ion-atom potential). They occur together, either as the ratio u_1/a (in the case of critical angles) or in summed analogous terms (in the case of minimum yields). In most substances, u_1 and a happen to be of a similar magnitude, but in diamond with its very low atomic number, u_1 is unusually small and a unusually large, giving a ratio u_1/a of about 0.17. Thus diamond represents an extreme case and can be expected to furnish a stringent test of currently accepted channeling theory.

That few diamond channeling experiments have been reported hitherto is probably due as much to the problems of obtaining consistent results with this material as to the problem of obtaining samples. Only three other groups[9–11] have published any critical-angle or minimum-yield measurements, and these investigations were not comprehensive.

It will be convenient to consider the minimum yield measurements first and in some detail. The critical angle measurements, therefore, will be considered in a subsequent companion paper, designated as II.[12] A preliminary description of these results has been published elsewhere.[13]

II. EXPERIMENTAL

A. Technique

Beams of protons and α particles were obtained from the accelerators of the Nuclear Physics Research Unit, a 2-MeV pressurized Cockcroft-Walton accelerator, and a 6-MV Tandem Van de Graaff accelerator. The beam, collimated to about $\frac{1}{20}$ of the expected axial critical angles at each energy, was incident on the diamond sample held in a two-axis goniometer of our own construction. Based broadly on a design of the Bell Laboratories, our goniometer included, however, some novel features of target translation and heating, which will be described separately.[14] A stepping-motor drive gave a smallest angular displacement at the target of 0.01 °. Backscattered ions were detected by a surface barrier detector of 16-keV FWHM (full width at half maximum) resolution placed at 155 ° to the beam direction, and the pulses fed via the usual electronics to a multichannel analyzer and scalers. The target was surrounded by a liquid-nitrogen-cooled shield to reduce contamination, and the ambient vacuum was $\sim 5\times 10^{-7}$ torr. Beam currents were a few nA on a 0.7-mm-diameter spot.

Each energy spectrum of the backscattered ions was converted to a "depth spectrum" using the range-energy relationship of Zaidins.[15] It was assumed that the channeled stopping power is equal to the random, the so-called "Aarhus convention"[16]; this is always a good average approximation for ions which are backscattered.

Channeled spectra were normalized by dividing them point by point by a spectrum for random incidence of the same ions. The random spectra were taken while continuously rotating the crystal, as suggested by Ziegler and Crowder,[17] taking care to avoid excessive influence from major axes. This should give a better random sampling than the often-used method of choosing a specific off-channel direction in which to take the random spectra. The suggestion[17] of using an amorphous target in inappropriate because chemical effects on stopping powers have been reported, notably for the carbon allotropes.[18]

Measurements of the same type were generally made on more than one stone to reveal any specimen dependence. However, this was small once careful attention had been paid to the precautions described below. Eight specimens were selected from 42 diamonds of good appearance, supplied to us by the de Beers organization. All but one were type-I*a* diamonds, but the type[19] (which is determined largely by point-defect phenomena) was not expected to significantly influence the channeling, with its dependence on long-range crystal order.

B. Precautions

The central problem of gathering channeling data on diamond is to obtain reproducible results from this natural crystal with its notoriously variable physical properties, dominated as they often are by small quantities of impurities or by lattice defects. Since diamond is the unstable form of carbon at ordinary temperatures and pressures, it cannot be refined by the usual thermal techniques, and simple selection must be used to get specimens representative of pure or intrinsic diamond.

An attempt was made to use x-ray topography and strain analysis under polarized light for this purpose, but the correlation with channeling measurements was poor. Presumably a perfect diamond would exhibit the lowest dechanneling and the lowest minimum yield, but it was not yet known how small a value to expect. However, an examination of many stones revealed a distribution of yields with a low-value cutoff (arrowed in Fig. 1) and a clustering of results just above this value, and the stones which fell in this region (below the dashed line) were concluded to be close to perfect crystals.

Rutherford backscattering of α particles showed that all the diamonds had a surface layer of impurities of various mass numbers, stones which had previously been in an untrapped diffusion-pumped vacuum system having particularly thick deposits of silicon and oxygen. Several solvents were tried as cleaning agents, including well-established hot acid processes.[20] The most convenient and thorough method was found to be ultrasonic agitation in a strong solution of the commercial product "Contrad" or "Decon 90." Further details of these investigations have been published.[21,22]

Methods of improving the channeling quality of the crystals and of regenerating them after deterioration due to radiation damage or beam-induced contamination were sought. The following techniques were investigated: gas etching by heating to 1000 °C in flowing CO_2,[23] conventional diamond gemstone polishing, annealing in UHV at about 1200 °C, ion milling with 800-eV Ar^+, and heating in hydrogen to 700 °C.[24] Gas etching, polishing, and annealing, all consistently made improvements (produced lower minimum yields[25]) with no unambiguous preference between techniques or the order in which they should be applied. Most of the eight selected stones were either gas etched, or polished and then annealed.

Radiation damage by an ion beam is fairly rapid in diamond, and subsidiary experiments were performed to evaluate its influence on the channeling measure-

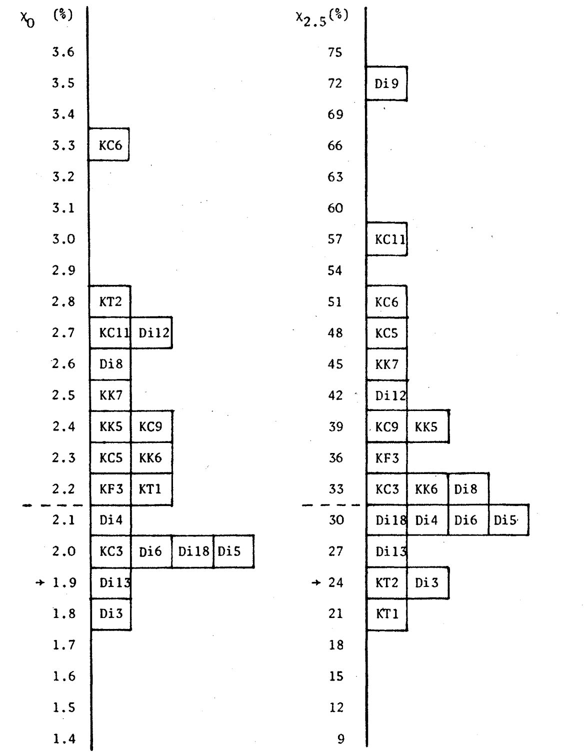

FIG. 1. Distribution of channeled minimum yields of various diamonds; χ_0 is the relative yield of protons backscattered just behind the "surface peak," and $\chi_{2.5}$ that of protons scattered at a depth of 2.5 μm.

ments. A quite extensive investigation of radiation damage ensued, and this work has been published separately.[26] Damage by proton beams was not observed even in the longest runs (maximum dose of $\sim 10^{17}$ ions cm^{-2}), and it was established that experiments using helium beams could be completed with ion doses (less than $\sim 3\times 10^{16}$ cm^{-2}) for which damage effects were negligible. In long series of experiments, the crystal was periodically translated to expose a fresh beam spot.

Ion beam experiments on insulators also suffer from the problem of target charging.[27] Not only does this present problems of current integration, but in the present experiments, it was found to deflect the incident beam significantly (up to 0.1°). The problem was solved by using a heated filament to flood the target with electrons and thus neutralize any positive charge buildup.

III. RESULTS AND DISCUSSION

A. General

Typical backscattered energy spectra for 1.0-MeV protons incident on a good diamond in major axial and random directions at room temperature are shown superimposed in Fig. 2. The spectra were analyzed to give two estimates of the minimum yield $\chi_{\min}$ at the surface: the yield χ_0 just behind the surface peak, as used in Fig. 1, and the yield χ_s extrapolated to zero depth by computer stripping of the surface peak. For accurate comparison with simple theories which neglect dechanneling, χ_s was used. The energy and ion dependence were found to be small in agreement with Eq. (1) below, and only the 1.0-MeV-proton results are considered in detail. Values of χ_s for the major axial and planar channels are listed in Table I.

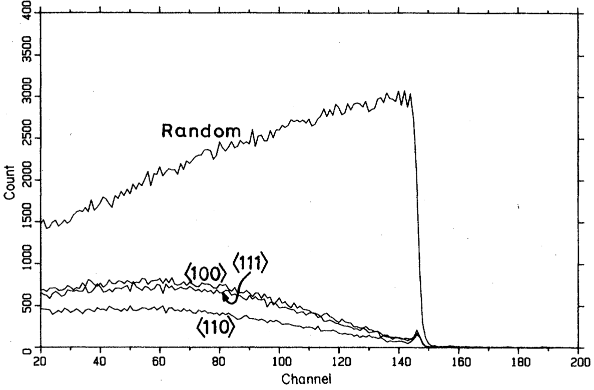

FIG. 2. Backscattered 1.0-MeV H^+ spectra, random and channeled incidence.

Subsurface oscillations in the spectra such as those observed by Roosendaal *et al.*[28] could not be seen here because their expected periodicity (about 300 Å) was less than the detector depth resolution (about 800 Å).

B. Surface peak

The number of counts in the surface peak was found to correlate with the beam exposure time and the crystal temperature, and was therefore due partly to a layer of amorphous carbon deposited from the

TABLE I. Channeled minimum yields in diamond at zero depth (χ_s) for 1.0-MeV protons, at room temperature.

Axis	$\chi_{\min}$(%)	Plane	$\chi_{\min}$(%)
⟨110⟩	1.5 ± 0.4	{110}	25
⟨111⟩	1.8 ± 0.2	{111}	32
⟨100⟩	2.2 ± 0.4	{100}	36

vacuum environment by beam-induced chemistry, as well as to the normal crystal surface contribution. An extrapolation of the surface peak content to zero beam exposure enabled the effective number of crystal surface atoms per atomic row perceived by the beam to be calculated by comparison with the height of the random spectrum[29]; the value was 6 ±1. The value calculated by the method suggested by Barrett [Ref. 8, Eq. (24)] lies between 4 and 6 for the range of temperatures used here (20 to 700 °C). The agreement is quite good, indicating that the crystal is perfect almost to the surface if prepared by one of the methods used.

A current theory of the polishing mechanism of diamond[30] is that of the tearing out by brittle fracture of small irregular blocks bounded mostly by the easy {111} cleavage planes. This would explain why so little damage is propagated into the bulk according to these and other[11] channeling experiments on polished diamonds (in contrast to metals). A thermally activated chemical mechanism[31] would, however, give a similar result.

Diamond of course has no amorphous surface oxide layer such as is found for example with silicon, the oxides of carbon being volatile. The chemistry of the diamond surface has received much speculation of late.[32] There is little evidence for the "dangling bonds" which would be produced by truncating the bulk structure, so they must either be eliminated by surface reconstruction (as is seen in some LEED experiments[33]) or be terminated by a layer of chemisorbed atoms. Even on freshly cleaned surfaces, Rutherford backscattering of helium ions always revealed an oxygen layer whose minimum atomic density corresponded to 1.2 ±0.1 monolayer (i.e., close to 1.0). It is suggested that after aqueous detergent cleaning the surface bonds are occupied by hydroxyl groups; evidence for the corresponding hydrogen layer has recently been seen.[34] On as-found diamonds the bonds may be satisfied by some of the other surface impurity atoms which were detected. After polishing alone, which is carried out in oily medium, it has been suggested[33] that a layer of hydrogen atoms bonds to the diamond surface.

C. Minimum yield

Barrett[8] fitted the following expression to the axial minimum yields in his computer simulations.

$$\chi_{\min} = Nd\pi(Cu_2^2 + C'a^2)(1+\zeta^{-2})^{1/2} + \chi_3 \quad . \qquad (1)$$

Here N is the number of atoms per unit volume, d is the string spacing, u_2 is the rms thermal vibration amplitude in two dimensions ($u_2 = \sqrt{2}u_1$), ζ is related to the effective number of crystal surface layers "seen" by the beam, χ_3 is the contribution from amorphous surface layers, C and C' are fitting parameters, and a is the Thomas-Fermi screening distance defined earlier.

The procedure proposed by Barrett for calculating χ_3 from the size of the surface peak[8] has never been fully checked experimentally, but the resulting values of χ_3 were in any case small enough (0.001 or 0.1% in most cases) to be regarded as a correction term. Much the same values were obtained from work on the effect of evaporated amorphous layers on diamond.[35] The factor $(1+\zeta^{-2})^{1/2}$ has been approximately verified[36]; it took values from 1.01 to 1.04 under the present conditions and could presumably be regarded as 1.00 to a good approximation. Equation (1) could therefore be rewritten

$$\chi_{\min} - \chi_3 = Nd\pi(Cu_2^2 + C'a^2) \quad . \qquad (2)$$

It is worth noting that with $C = C' = 1$, this is the expression which was tentatively proposed by Lindhard,[3] the two right-hand terms being his χ_1 and χ_2 respectively. It predicts $\chi_1 \sim \frac{1}{4}\chi_2$ in most substances, so that χ_1 was often neglected in early experimental comparisons — an approach which is still occasionally encountered in the literature.

Barrett[8] found that the best-fit values were in fact

$$C = 3.0 \pm 0.2, \quad C' = 0.2 \pm 0.1 \quad ,$$

and these values result in χ_1 predominating greatly over χ_2 in most substances, where $u_2 \sim a$. In fact one can usually take $C' \simeq 0$; moreover it is difficult to determine any more accurate value for C' experimentally. But in diamond $u_2 \ll a$, and χ_1 and χ_2 have comparable values, enabling C' to be investigated.

The expected proportionality at a fixed temperature of $\chi_{\min} - \chi_3$ to d is confirmed in Fig. 3 (note that these particular data were averaged over a greater depth than those in Table I and the absolute values are therefore greater). A plot of $(\chi_{\min} - \chi_3)/d$ vs u_2^2 should then be a straight line, enabling C and C' to be determined from the slope and intercept, respectively.

Such a plot is presented in Fig. 4, with u_2 calculated by standard Debye theory, taking the Debye temperature for diamond as 1860 ±10 K.[37] Although there is considerable scatter, the trend is clear, with no systematic deviations for any of the three major axes. A least-squares regression (included on the graph) gives

$$C = 3.2 \pm 0.6, \quad C' = 0.05 \pm 0.05 \quad .$$

These results are quite interesting. The value of C is very similar to Barrett's, while C' is rather less, and approaches (but is probably not equal to) zero. Similar values have been obtained by, for example, Komaki *et al.*[38] with protons on silicon. It is of particular interest that even in diamond, where u_2 is much smaller in comparison with a, that the thermal

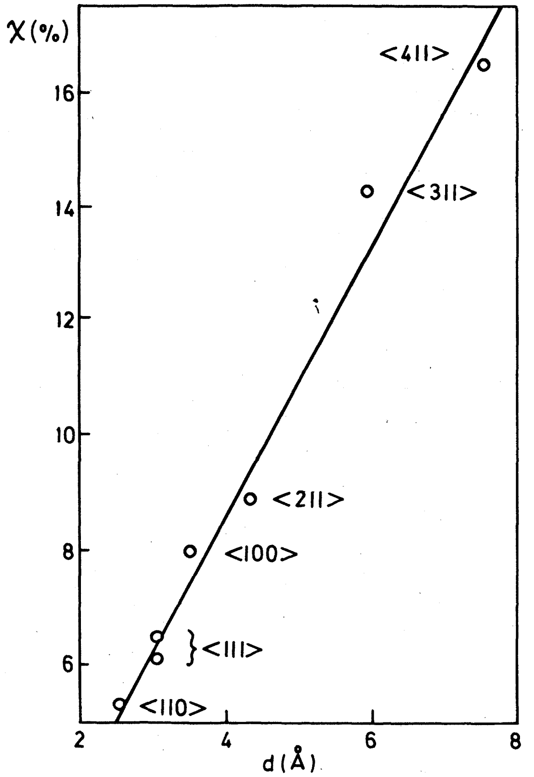

FIG. 3. Depenence of axial minimum yield on the string spacing *d*.

term still plays the major role in determining minimum yields.

It was formerly common to interpret the minimum yield as arising from the "forbidden zone" around each atomic row. Barrett[8] showed that this simple geometrical model is untenable, and that a significant contribution to $\chi_{\min}$ comes from those trajectories which do not have sufficient transverse energy to approach the rows. Such trajectories still have a finite nuclear encounter probability, and are very numerous. The temperature dependence of $\chi_{\min}$ comes in this model from the temperature dependence of the density-of-trajectories function defined by Barrett and derived from the potential for a vibrating row; the dominance of χ_1 over χ_2 is enhanced by the focusing of trajectories on to neighboring rows according to the lattice geometry.[39] The present results confirm the validity of this approach.

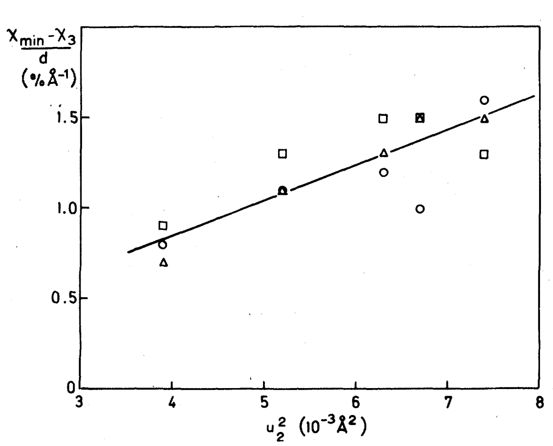

FIG. 4. Graph giving temperature dependence of axial minimum yield: ○⟨110⟩, Δ⟨111⟩, □⟨100⟩.

No general relationship analogous to Eq. (1) has been proposed for the minimum yields in planar channeling, other than a rough estimate due to Lindhard[3]:

$$\chi_{\min} \sim 2a/d_p \ , \tag{3}$$

where d_p is the interplanar spacing. This formula underestimates the $\chi_{\min}$ values for most substances and overestimates them for diamond, although the data in Table I show quite good d_p^{-1} proportionality. It is evident that a more complex relationship than Eq. (3) is required, probably including a thermal term. A relationship of the form

$$\chi_{\min} = 2(Bu_1 + B'a)/d_p \tag{4}$$

might be appropriate. The planar data of the present work showed only a small temperature variation, and B and B' could not be fitted accurately; values of $B \gtrsim 1$ and $B' \lesssim 1$ are consistent with these data and with those of Roosendaal *et al.*[40] (Si) and of Davies *et al.*[41] (Si, W, and Au). Barrett's computer simulations for W, presented graphically,[8] require $B = 2.2$ and $B' = 0.6$.

Values of χ_0 for 1.0-MeV protons incident along ⟨110⟩ in diamond have been reported by Picraux *et al.*[9] (4%) and by Sellschop and Gibson[10] (2.1%); a value for ⟨111⟩ alignment, which should be about 20% greater than that for ⟨110⟩, has been reported for 0.35-MeV protons by Braunstein *et al.*[11] (5.5%). A comparison with Fig. 1 indicates that only Sellschop and Gibson's diamond was of comparable quality to the ones used in the present work.

IV. SUMMARY

It has been shown that although it is difficult in diamond to obtain consistent ion-channeling data which reflect the ideal crystal structure rather than its defects, this can be achieved with care. The surface-peak data confirm that the crystals used were quite perfect almost to the surface, and support some existing ideas as to how a diamond terminates itself naturally at a free surface. It would appear that impurity atoms ensure that the much-vaunted "dangling bonds" do not arise. The data for polished specimens are consistent with current theories on the mechanisms of diamond polishing.

The channeled minimum-yield measurements agree rather well with the predictions of Lindhard[3] or of Barrett[8] as regards the weakness of the ion and energy dependence, and the form of the row or planar spacing dependence. The temperature dependence of $\chi_{\min}$ for axes is in accordance with Eq. (1) (which summarizes the Monte Carlo simulations of Barrett[8]); the low u_1/a ratio for diamond enables a fairly accurate value for the small constant C' to be extracted. This is even closer to zero than previously suggested[8] and confirms that the simple geometrical model for the interaction of a channeled ion beam with the atomic rows is not a good description.

In the case of planar minimum yields, only a simple geometrical prediction [Eq. (3)] is available, and it disagrees with the data in absolute values and in the lack of a temperature dependence. A tentative suggestion is made for a more suitable form of relationship [Eq. (4)], but this can only be tested for a crystal in which the value of u_1/a at accessible temperatures is greater than it is in diamond.

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