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DETECTION OF FOREIGN ATOM SITES BY THEIR X-RAY FLUORESCENCE SCATTERING*

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The position of a solute atom in a lattice can be detected by the nature of its x-ray fluorescence excitation during a diffraction process.

The determination of the interstitial or substitutional nature of impurity atoms in crystalline solids has been given impetus recently because of particle channeling experiments. We wish to report here a rather direct method of determining the lattice position of a foreign atom by observing the fluorescence emitted by the atom during a diffraction process. Although the method, as illustrated by the present experiment, is limited to particular combinations of solute atoms and host lattices, in principle it can have much wider application.

When an incident beam is Bragg reflected by a reasonably perfect crystal, a standing-wave pattern is set up in the crystal which causes a change in the field intensity at a lattice site with respect to the average field of the incident plane wave when no diffraction takes place. This effect, which is explained by a two-beam dynamical theory, is responsible for the anomalous transmission or Borrmann effect in x-ray transmission. In this transmission case, a nodal plane of the electric field forms at the atom sites and the cross section for photoelectric loss (which is the primary absorption process) is reduced drastically. In the reflection case, as the incident angle increases from values smaller than the Bragg angle, there is a reduction of intensity at the atom sites resulting in a node of in-

tensity when the region of total reflection is reached. On the high-angle side of this region, there is an antinode of the field intensity at the atom site which gradually reduces to the incident-beam plane-wave values at large angles of incidence.

The nodal plane is precisely that which would be formed by the superposition of two plane waves in space such that wavelength (λ) and angle between their propagation directions (2θ) are related by Bragg's law, $\lambda = 2d_{hkl}\sin\theta$, and the spacing of the planes d_{hkl} is just the spacing of the nodal planes.

At certain interstitial sites for particular reflections the node-antinode situation will be reversed with respect to a lattice site. Hence, by observing the fluorescence of characteristic radiation from the solute atom as a function of Bragg angle, the location of the solute can be determined.

To demonstrate these ideas experimentally we used a highly perfect silicon single crystal heavily doped with arsenic.¹ The resistivity was 0.002 Ω cm and corresponded to an arsenic concentration of about 5×10^{19} cm⁻³. The experimental arrangement shown in Fig. 1 was similar to a previous experiment² used to detect the fluorescence from the host lattice and thus demonstrate the presence of the nodal and antinodal

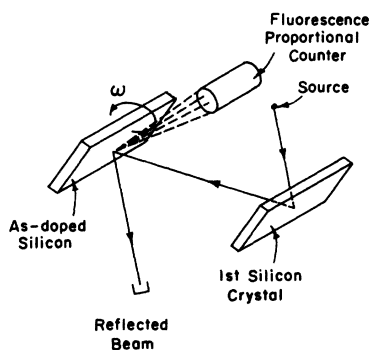


FIG. 1. Double crystal arrangement. The second crystal is rotated with uniform angular velocity ω through the reflection region. The As fluorescence approximately normal to the plane of incidence is detected with the proportional counter.

wave fields. The incident radiation was $\text{Mo } K\alpha$ ($\lambda = 0.71 \text{ \AA}$) which could readily excite arsenic K fluorescence of $\lambda \approx 1.1 \text{ \AA}$. The silicon fluorescence is not detected because of its long wavelength. The scattering from the doped silicon consists of $\text{Mo } K\alpha$ (produced by phonon and Compton processes) and the arsenic K fluorescence. The resolution of the proportional counter is about 15% in the 1- \AA region. Using a multichannel analyzer we were able to show definitely that the radiation in the vicinity of 1.1 \AA was from arsenic. (We were just able to resolve the separate $\text{As } K\alpha$ and $K\beta$ peaks.) The data were taken with a single-channel analyzer set to accept the $\text{As } K$ lines. With the window thus set, only 1/150 of the $\text{Mo } K\alpha$ thermal scattering is detected. Only the fluorescence leaving the crystal at small glancing angles was recorded. This is of low intensity because of high self-absorption in the specimen but has a larger degree of asymmetry than radiation leaving normal to the surface. (The reason for this is given in Ref. 2.) The $\text{As } K$ fluorescence was the order of 10 counts/sec and the $\text{Mo } K\alpha$ getting through the single-channel analyzer was $\approx \frac{1}{2}$ count/sec. The fluorescence intensity normal to surface was about 10 times greater.

Figure 2 is a chart recording consisting primarily of the As fluorescence taken while the crystal is rotated through the angular range of the (220) reflection. The shape of the actual (220) peak is shown in the inset. The latter is the symmetric curve expected from the convolution of two Darwin-Prins curves. The fluorescence curve is markedly asymmetric with lower intensity at the low-angle side. On this side of

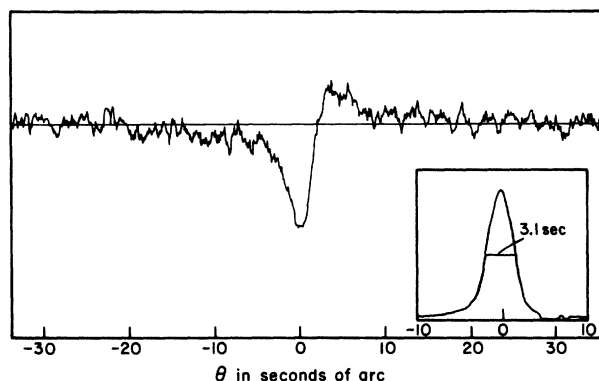


FIG. 2. A tracing of a chart recording of the arsenic fluorescence recorded while the crystal was rotated through the (220) reflection. The entire recording took about 8 h. The inset shows the (220) diffracted beam which occurs simultaneously with the dip in the fluorescence curve.

the reflection a diminution of wave-field intensity takes place in planes containing the lattice sites. The low arsenic scattering is consistent with arsenic atoms lying on the (220) atomic planes containing the silicon host atoms, but does not differentiate substitutional or interstitial sites lying within these planes.

The most likely interstitial sites in silicon are obtained from lattice sites by translations of the type $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ all of which lie on (220) planes. A measurement of fluorescence associated with the (111) Bragg planes would in principle show a different asymmetry if these interstitial sites were occupied. The wave-field distribution in the crystal, however, is not quite as straightforward with the (111) as it is with the (220) reflection. Consideration of the diamond structure shows that Miller planes spaced d_{111} do not include all the atoms, i.e., if a particular (111) plane of atoms is coincident with a Miller plane (111), half of the atoms will lie on parallel planes $\frac{1}{4}$ of the distance to the next (111) plane. It is for this reason that the structure factor for (111) is $32^{1/2}$ and not 8—the latter applying for those reflections where all the atoms scatter in phase such as (220). In this case, the nodal plane of the wave field can be shown³ to pass through the centers of symmetry lying half-way between adjacent (444) planes of substitutional atoms. Furthermore, on the low-angle side of the total-reflection region the field intensity at the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ interstitials is approximately $(1 + \frac{1}{2}\sqrt{2}) / (1 - \frac{1}{2}\sqrt{2}) = 5.8$ greater than at substitutional sites with the inverse being the case at the high-angle side. It

follows, then, that if the arsenic is substitutional, its fluorescence for (111) diffraction should have the same asymmetry as in Fig. 2, but not as pronounced. This was indeed the experimental observation, and is consistent with the conclusion that the arsenic atoms lie on substitutional sites.

The present method is not limited to x-ray diffraction but can be applied to neutron diffraction where a capture process results in the emission of a detectable particle. This would allow light elements to be detected (for example, lithium in silicon) and would extend the range of possible host-solute combinations. The method is limited to reasonably perfect crystal specimens. It may

be possible, however, to use that part of the fluorescence which takes place in a diffraction process to identify the site of the fluorescing species even if the crystal is not perfect.⁴

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DIELECTRIC CLASSIFICATION OF CRYSTAL STRUCTURES, IONIZATION POTENTIALS, AND BAND STRUCTURES

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It is shown that dielectrically defined average covalent and ionic energy gaps, E_h and C , respectively, can be used to predict crystal structures and absolute band energies in crystals of formula AB with eight valence electrons per atom pair.

A great many crystals AB containing eight valence electrons per atom pair are known. These range from semiconductors like Si and Ge to ionic crystals like NaCl. Thermochemical data show¹ that the differences in energy for some of these crystals between the "ionic" NaCl structure and the "covalent" zinc-blende structure are as small as 1 kcal/mole. Calculations based on the Born closed-shell model¹ of the cohesive energies of partially ionic crystals are typically in error by 10 kcal/mole, and no accurate method is known for including covalent energies. Thus theoretical predictions of the relative stability of the NaCl and zinc-blende structures have generally been unsuccessful from a quantitative point of view,¹ even when confined to I-VII crystals.

In this note we show that the entire range (IV-IV, III-V, II-VI, and I-VII) of AB crystals can be analyzed dielectrically, using an open-shell energy-band model (random-phase approximation) rather than the Heitler-London picture implicit in the Born model. We begin by defining fractional covalent and ionic characters f_c and f_i of the crystalline cohesion in terms of the average covalent and ionic energy gaps E_h and C defined previously.² Values of E_h and of C have been

tabulated for 68 AB crystals.^{3,4} From these one can calculate f_c and f_i from the definitions

$$f_c = \frac{E_h^2}{E_h^2 + C^2}, \quad f_i = \frac{C^2}{E_h^2 + C^2}. \quad (1)$$

Representative values for f_c are given in Table I for 28 crystals; of course, $f_i = 1 - f_c$. It is seen that the crystals under consideration range from 100% covalent to 96% ionic.

From the table one can see that, as expected, the more ionic crystals have the NaCl structure, while the less ionic ones occur in the zinc-blende or diamond structures. The dividing point between octahedral and tetrahedral coordination is $f_i = 0.785 \pm 0.010$. We have displayed in Fig. 1 the two dimensional population distribution in the $C - E_h$ plane. It is seen that there are three separate regions. In two of these the crystals have (A) the NaCl structure or (D) the diamond or zinc-blende structure. Between these two regions there is a narrow region (B) where wurtzite structures occur.

To understand the microscopic origin of the boundaries between these regions it is convenient to determine the energy of valence-band