Preferred Sites of Impurities Implanted in Be: Lattice Location and Quadrupole Interactions

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The quadrupole interaction of the 247-keV level of ^{111}Cd in a Be host is observed to differ by a factor of 3.4 depending on whether the sample is prepared by the implantation of the parent radioactivities ^{111}Ag or ^{111}In. Ion-channeling measurements have shown this difference to arise from the preference of implanted Ag to reside in substitutional sites and In in the tetrahedral interstitial sites of the Be lattice.

Measurements of the nuclear quadrupole interaction (QI) at ^{111}Cd embedded in several noncubic metallic host lattices have been performed recently in this laboratory.[1] The time-dependent perturbed-angular-correlation (TDPAC) technique was applied to study samples prepared by radioactive-ion implantation of the parent isotopes ^{111}Ag or ^{111}In. The measured QI of the daughter nucleus ^{111}Cd was, in all instances but one, independent of the choice of ^{111}Ag or ^{111}In as parent. The one anomalous case, that of a Be host, is the subject of this Letter. We have found through use of the ion-beam channeling technique[2] that Ag and In, when implanted into Be, come to rest at different positions in the hcp Be lattice. In particular, Ag resides completely on regular substitutional sites whereas the unique site occupied by In is the regular tetrahedrally coordinated interstitial site. This represents the first definitive observation, to our knowledge, of an implanted metallic impurity at a simple unique interstitial site in a metallic host.[3] As a consequence of the different site preferences of ^{111}Ag and ^{111}In, we have also obtained the first QI measurement for the same impurity nucleus (^{111}Cd) at both a substitutional and an interstitial site in the same host lattice. A comparison of the measured QI values with electric field gradients (EFG) calculated from a simple point-ion lattice sum implies that the total QI (lattice plus electronic contributions) is proportional to the lattice field with the *same* proportionality factor at both sites.

Details of the application of β-γ and γ-γ TDPAC techniques to the measurement of the sign and magnitude of the QI at ^{111}Cd have been described elsewhere.[4,5] The parent radioactive species, ^{111}Ag and ^{111}In, were implanted at an energy of 90 keV into a Be single crystal of 1 cm^2 area and $\frac{1}{2}$ mm thickness using the Princeton isotope separator. The hexagonal $\hat{c}$ axis was oriented in the plane of the crystal which was chemically cleaned before each implantation. Figure 1 shows the delayed β-γ coincidence spectrum obtained using

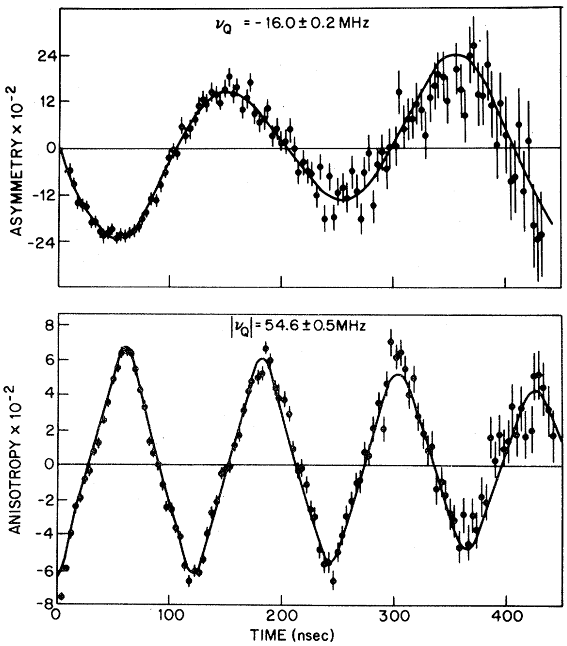

FIG. 1. Upper portion: quadrupole-precession modulation of the delayed β-γ coincidence spectrum for ^{111}Ag implanted in Be. Lower portion: quadrupole-precession modulations of the delayed γ-γ coincidence spectrum for ^{111}In implanted in Be. Both precessions refer to the 247-keV level of ^{111}Cd daughter.

the Ag parent and the γ-γ spectrum for the In parent. The resulting quadrupole coupling constants $\nu_Q = e^2qQ/h$, obtained from least-squares fits to the data, are $\nu_Q = -16.0 \pm 0.2$ MHz and $|\nu_Q| = 54.6 \pm 0.5$ MHz, respectively, differing by a factor of 3.4. This was the first indication that Ag and In implantation in Be may populate different lattice sites. We can infer from the shape of the observed spectra that the symmetry axis of the interactions is the $\hat{c}$ axis of the Be crystal. The amplitude of modulation using the ^{111}In parent however was only half that expected if all Cd nuclei had experienced the same unique QI.

The assignment of each value of ν_Q to a corresponding lattice site was made on the basis of channeling[2] measurements performed on the same Be crystal after implantation of $\sim 5 \times 10^{14}$/cm^2 Ag ions on one side and the same dose of In on the other. Rutherford-scattering yields of 1.8-MeV He$^+$ ions from the Be host and from the heavier impurity (Ag or In) were measured as a function of the angle made by the well-collimated incident beam to various symmetry directions of the crystal. The results, displayed in Fig. 2, show that the normalized yields from Ag and the Be host lattice are essentially identical along the (0001) plane and $\langle 11\bar{2}0 \rangle$ axis, which implies *complete* substitutional site occupation for the Ag.

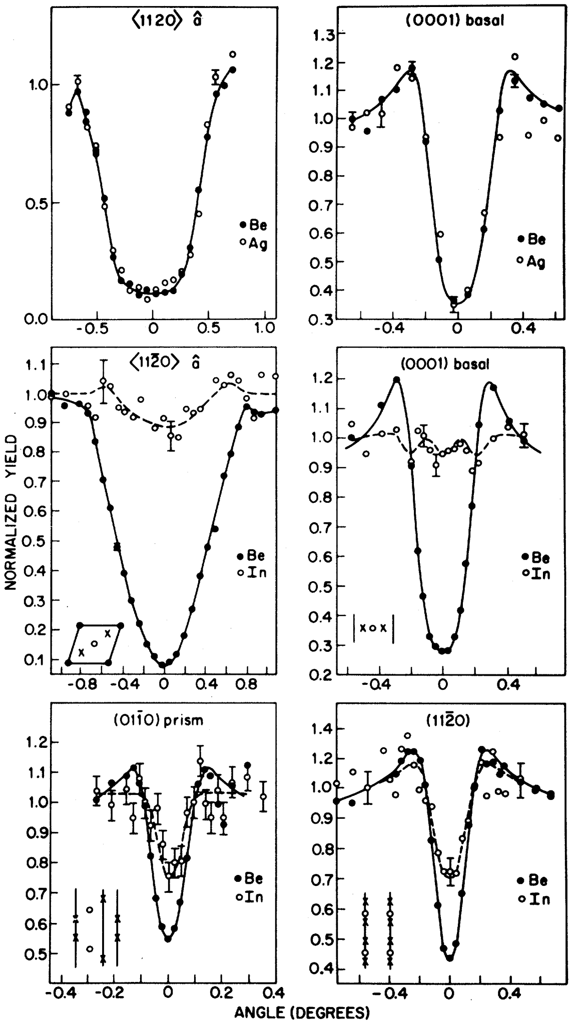

FIG. 2. Top: scattering-yield angular scans about the $\hat{a}$ axis and basal plane for Ag in Be. Middle and bottom: angular scan about four channeling directions for In in Be. The insets show the projections normal to the indicated channel of the octahedral (circles) and tetrahedral (crosses) interstitial sites.

Figure 2 also shows that the angular scans for the In impurity about these two channels are, on the other hand, flat to within the statistical accuracy of the data, which clearly shows that In implants do not occupy substitutional sites in Be. The insets in the figure show the projections normal to the channeling direction of the two most likely regular interstitial sites in the hcp structure[6]; viz., the octahedral and the tetrahedral sites. Since these both fall within the (0001) and $\langle 11\bar{2}0 \rangle$ channels, the In data for these directions do not distinguish between the sites. Two additional crystal planes were therefore scanned, the (01$\bar{1}$0) and (11$\bar{2}$0), where it can be seen that the tetrahedral site appears substitutional (i.e., it lies in planes of host atoms) in both but the octahedral site is visible in the (01$\bar{1}$0) channel center. The data for these cases, which clearly show equal reductions in yield for both planes, rule out the octahedral site and are consistent with about 50% occupation of the tetrahedral site and 50% of "random" sites, since the reductions in yield are about half that of scattering from the host. Since the amplitude of modulation of the TDPAC spectrum for the ^{111}In parent was only half of that which would have been observed if all daughter ^{111}Cd nuclei were in the unique site, we can associate that site with the tetrahedral interstice. The remaining 50% of the In nuclei are assumed trapped in regions of lattice damage where widely distributed values of the quadrupole coupling can be expected, thus accounting for both the loss of amplitude in the TDPAC spectrum and the 50% "random" fraction observed in channeling.

Two additional TDPAC measurements, the details of which will be found in a forthcoming complete description of this work, are relevant to the present discussion. The QI at ^{111}Cd in Be determined using a source prepared by implantation of ^{111m}Cd as the parent isotope was found to be identical to that obtained using In implantation. This shows that implanted Cd also prefers the tetrahedral interstitial site. The sign of the QI at this site was inferred to be negative from a β-γ TDPAC measurement using implantation of ^{115}Cd in Be. Although the latter experiment actually determines the sign at ^{115}In in Be, we believe the sign at Cd and In is the same, as was found previously for a Cd metal host.[4] Thus the EFG has the same sign at the substitutional as well as interstitial sites.

Comparison of the channeling and TDPAC results allows us to associate the larger QI frequency with Cd at the interstitial site and the smaller with substitutional Cd. One can attempt to derive a qualitative understanding of this large difference in the frequencies at the two sites by estimating the contribution of the lattice of positive ions to the EFG at each of these two sites using a straightforward summing procedure.[7] However, the precise lattice position of the tetrahedral interstitial site is only known from symmetry considerations in the ideal hcp lattice ($c/a = \sqrt{\frac{8}{3}}$). Since the axial ratio of Be ($c/a = 1.5677$) is not ideal, we must take the distance of this site from the basal planes as an unknown parameter. In Fig. 3, the ratio of the lattice EFG at the tetrahedral site to that at a substitutional site is plotted against this parameter. It can be seen that the experimental ratio of field gradients, if taken at face value, corresponds to a location of the tetrahedral site slightly closer to the basal planes than in an ideal hcp lattice. This is consistent with the axial ratio of Be being less than ideal, which would displace this site toward the basal planes. Such agreement admits the possibility that the *total* field gradient is proportional to the host-ion lattice contribution with the *same* proportionality constant at each site. In view of the severe lattice distortions to be expected around an interstitial impurity, this simple result is surprising.

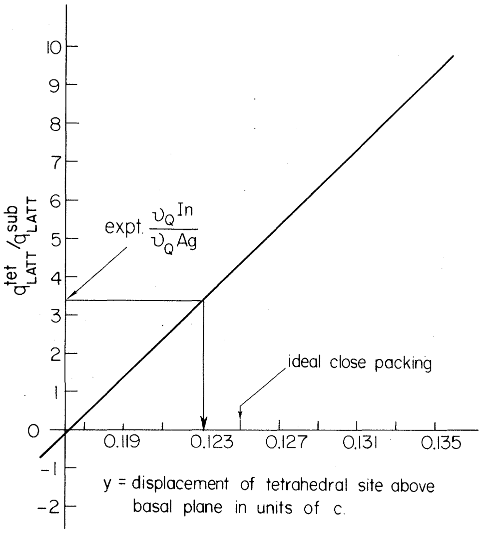

FIG. 3. Ratio of the EFG at the tetrahedral interstitial site to the substitutional site as derived from lattice sum calculations versus the distance of the tetrahedral site from the basal planes (in units of the lattice constant c).

We can make the following comments on the lattice location in Be of implanted Ag on the one hand and In (or Cd) on the other. Studies of binary-alloy systems[8] involving Be have indicated no solid solubility with either In or Cd. The data for Ag, on the other hand, show limited solubility at high temperature (e.g., 0.045 at.% at 1000°C) and extrapolate to $\sim 10^{-4}$ at.% at room temperature. An average local impurity concentration of at least 0.05 at.%, applicable to the present study, is thus far in excess of the room-temperature solubility of Ag in Be. In spite of this the Ag appears completely substitutional and not coordinated with lattice damage. The Ag-Be phase diagram is typical of systems in which the two components are chemically compatible but incompatible in size.[9] The amount of solute which can be accommodated is limited by overall lattice strain energy of the solvent. We can envision the Ag-implantation process as one in which the Ag ion comes to rest at the end of range in a region of short-lived high effective temperature created by the energy deposited by the Ag ion itself.[1] The high local temperature allows the Ag to occupy a substitutional site without regard for *long-range* lattice strain due to other Ag atoms. The rapid dissipation of the temperature spike effectively freezes the impurity in place, a process analogous to rapid quenching from high temperature. In the case of In (or Cd), assuming that they show no macroscopic solubility in Be because of a chemical incompatibility, they apparently avoid available substitutional sites in order to reduce the *local* chemical energy and find themselves frozen into regions of disorder and the interstices of the lattice. Why such a large fraction of these impurities prefer to reside in the tetrahedral interstice is at present an open question.

From the point of view of studying hyperfine interactions in ion-implanted samples, which is widely practiced now, this work indicates the need for caution in ascribing the observation of unique final sites of impurities automatically to substitutional lattice sites. The effectiveness and value of combining lattice-location techniques with hyperfine-interaction studies is clearly brought out with renewed emphasis.

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[3] The obvious exceptions to this are light elements of the first and second periods which are known to form interstitial compounds with the heavier metals.

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Low-Temperature Metallic Behavior and Resistance Minimum in a New Quasi One-Dimensional Organic Conductor*

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The dc and microwave conductivities of the new organic charge-transfer salt hexamethylene-tetraselenafulvalinium tetracyanoquinodimethanide (HMTSF-TCNQ) remain metallic in magnitude to temperatures at least as low as 1.1 K. At low T we observe a resistance minimum and thermoelectric anomaly consistent with the theoretical result that density fluctuations can enhance the resistivity of a one-dimensional metal as $T \rightarrow 0$. Implications for $(SN)_x$ and tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ) are discussed.

We report the first organic material which behaves electrically as a metal throughout the temperature range 1.1–300 K. The new compound hexamethylene-tetraselenafulvalenium tetracyanoquinodimethanide (HMTSF-TCNQ) (Fig. 1) is an addition to the class of quasi one-dimensional conductors based upon the prototype TTF-TCNQ.[1]

The synthesis and chemistry of HMTSF-TCNQ are presented elsewhere.[2] Electronically, the new donor molecule is indistinguishable from its tetramethyl analog, TMTSF,[3] whose triclinic TCNQ salt becomes insulating below 70 K.[4] Sterically, however, the larger, nonplanar HMTSF is incompatible with the crystal structure[4] of TMTSF-TCNQ. Instead, HMTSF-TCNQ is nearly orthorhombic,[5] with a density of chains per unit area about 20% lower than that of TTF-TCNQ. The structure is disordered along one principal direction perpendicular to the stacking axis.[6] The higher symmetry, reduced interchain