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Equilibrium positions of Au atoms in Sn crystals as determined by a channeling technique*

J. W. Miller,[†] D. S. Gemmell, R. E. Holland, J. C. Poizat,[‡] J. N. Worthington, and R. E. Loess[§]
Argonne National Laboratory, Argonne, Illinois 60439

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The lattice location of Au atoms diffused into Sn monocrystals has been studied under equilibrium conditions at 217 °C by channeling and backscattering techniques using a 2.5-MeV Ne beam. The results show that the Au atoms dissolve almost entirely in substitutional positions, so that the unusually fast lattice diffusion of Au in Sn is most likely due to a very small fraction of Au atoms migrating interstitially.

I. INTRODUCTION

The diffusivity of the noble metals in many polyvalent host crystals is many orders of magnitude larger than that of ordinary lattice diffusion which is believed to occur entirely by the vacancy mechanism.[1–3] Several experiments have shown that an interstitial type of mechanism is required to explain both the anomalously high diffusivities and the lack of enhancement of self-diffusion by impurity additions.[4,5] A common feature of the diffusional behavior of coinage metals in these cases is that Cu generally diffuses much more rapidly than Au, and Au more rapidly than Ag. This behavior suggests that these metals diffuse by the dissociative mechanism that was successful in explaining the similar unusual behavior of Cu in Ge.[6] In the general case, this mechanism implies that equilibrium is maintained between several impurity defects, such as simple interstitials or substitutional atoms. Diffusion experiments of various types have suggested the types of impurity defects involved, but more conclusive evidence as to the site location of such impurities is required to interpret the findings. In this paper we report quantitative evidence as to the equilibrium site locations of Au dissolved in Sn by use of channeling techniques.[7–11]

Most of the atom-location measurements reported in the literature thus far have been made on samples in which the impurities have either been introduced by ion implantation or "frozen in" by quenching from high temperatures where the solubility limit is high. Most interesting cases for the site-location studies are those for which the impurity is believed not to be entirely substitutional, and is also only slightly soluble at the sample temperatures commonly achievable in channeling measurements (up to a few hundred degrees centigrade). In these cases impurity concentrations sufficiently high that channeling techniques are practicable (typically $\gtrsim 0.1$ at.%) are usually well above the solubility limit; metastable conditions such as implanting or "quenching in" are then used to attain high enough concentrations.

It is therefore worth noting that the solubility limit of Au in Sn is high enough that the equilibrium lattice positions of Au may be studied at modest temperatures, and that the lattice diffusion of Au in Sn is believed to occur predominantly by migration of intersititial defects.[12] The solubility of Au in Sn reaches a value[13] of ~0.2 at.% at a temperature of 200 °C, and is likely to be somewhat higher at the eutectic temperature of 217 °C. The measurements to be reported here were made for Sn (Au) crystals maintained at 217 °C, in which the diffused Au was nearly homogeneous at a concentration somewhat less than the maximum solubility.

II. TECHNIQUE

Our initial approach was to measure the orientation dependence of the characteristic Au x rays induced by 1-MeV proton bombardment. A Si (Li) detector was used. The intense x rays from Sn were successfully filtered out using thin Rh and Pd absorber foils. There was still insufficient sensitivity, however, because of the background radiation. Since the method also compares poorly with backscattering techniques as regards depth sensitivity, the attempt was abandoned in favor of ion-backscattering techniques.

The technique finally adopted was the measurement of backscattering of a 2.5-MeV ^{20}Ne beam accelerated in the Dynamitron at Argonne National Laboratory. Use of an ion as heavy as Ne permitted an adequate kinematical separation between the energies of ions backscattered at 157.5° from Sn and Au in the first few thousand angstroms of a thick target crystal. Figure 1 shows a typical backscattering spectrum obtained with a surface barrier detector. Antipileup circuitry was used (and, in fact, was essential) to permit the measurements to be made in a reasonable period of time. The details of the channeling apparatus have been previously published.[14] The angular divergence of the beam at the target was ± 0.03°, the beam spot diameter was 1 mm, and the approxi-

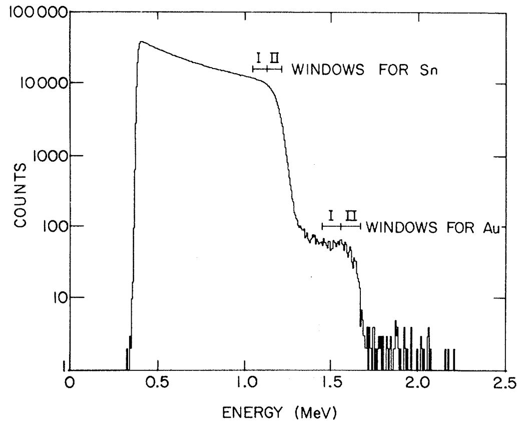

FIG. 1. Energy spectrum of ^{20}Ne ions backscattered at 157.5° from an Sn (Au) crystal maintained at 217°C under equilibrium conditions. The incident beam energy was 2.5 MeV, and the crystal was not aligned in a channeling direction. The two sets of energy windows correspond to the sets of data shown in Fig. 2.

mate vacuum during the measurements was $\sim 10^{-6}$ Torr.

The Sn crystals were spark cut to particular orientations from a single-crystal ingot grown from the melt of nominally 99.9999%-pure Sn, obtained from Cominco American, Inc. Initial orientation was performed utilizing the symmetry of optical reflections from etch pits,[15] and final determinations made using Laue x-ray patterns. Samples were then electropolished using concentrated HCl to remove damaged surface layers. The resultant wafers were about 1 mm thick and 5 mm in diameter, and were usually so oriented that one of the major crystal axes lay within a degree or two of the normal to the circular front surface. The back surface of each sample was then cemented to a target holder by means of a thermally and electrically conductive Epoxy.

After masking with an appropriate lacquer, gold was electroplated onto the back surface of each Sn sample (through a hole in the target holder), using a cyanide plating bath. Diffusion anneals were carried out at 209 °C for a sufficient length of time to permit near homogeneity to be attained, at a concentration slightly less than the maximum solubility. Normally, several plating and diffusion sequences were performed in order to attain the saturation concentration of Au for this temperature. Any excess gold remaining after the final diffusion anneal was removed by etching, and targets were stored in a vacuum oven at 217 °C until immediately before use in the channeling experiments.

After rapid transfer to the channeling target chamber, each sample was again heated to and maintained at 217 °C. In this condition, target Sn samples contained a practically homogeneous distribution of Au at nearly the maximum possible concentration, so that both redistribution and precipitation of Au were avoided. Furthermore, in accord with our findings concerning the temperature dependence of radiation-damage effects during channeling experiments in pure Sn,[16] radiation damage is able to anneal continuously during experiments at this temperature, and implanted Ne ions are able to out-diffuse; the formation of bubbles, blisters, and any other damage detectable by channeling measurements is thus avoided. As a check that damage problems were not incurred, axial spectra were periodically measured and checked against earlier spectra for any signs of damage. In addition, visual checks were made *in situ* using the accessory microscope.

In order to permit determination of interstitial fraction, interstitial site(s), and related flux-peaking effects[17,18] for the Au impurity, detailed angular scans were made of several major crystalline planes and axes. The statistics of counting for these scans were such that an interstitial fraction of about 5% should be detectable. Flux peaking effects might allow detection of an even smaller fraction.

III. RESULTS

The detailed angular scans for both planes and major axes were first corrected for dead time. Residual pileup was corrected for by comparison with similar spectra for pure Sn, as a function of count rate. The resultant pileup corrections for the spectra of particles backscattered from Au atoms were 10% or less. The Ne-beam current during these measurements was approximately 10 nA, and the detector resolution, as determined by backscattering of protons from a thin foil consisting of C, In, and Au layers, was approximately 15 KeV. Energy discrimination windows were then chosen for particles backscattered from either Sn or Au, from 0 to 300, and from 300 to 600 Å, labeled II and I, respectively, in Fig. 1. The quoted depth scales are based on the energy loss for Ne in Sn in a "random" direction,[19] and the appropriate kinematic losses were taken into account. These depth discriminations are referred to as "surface" and "deep," respectively, in the angular scans presented in Fig. 2. Finally, all backscattered yields were properly normalized with respect to an experimentally determined "random" yield. The ratios of "random" yields from Au and Sn were also corrected for their relative Rutherford scattering cross sections to obtain the concentration of Au dissolved in these Sn samples. Thus the solubility limit of Au in Sn was

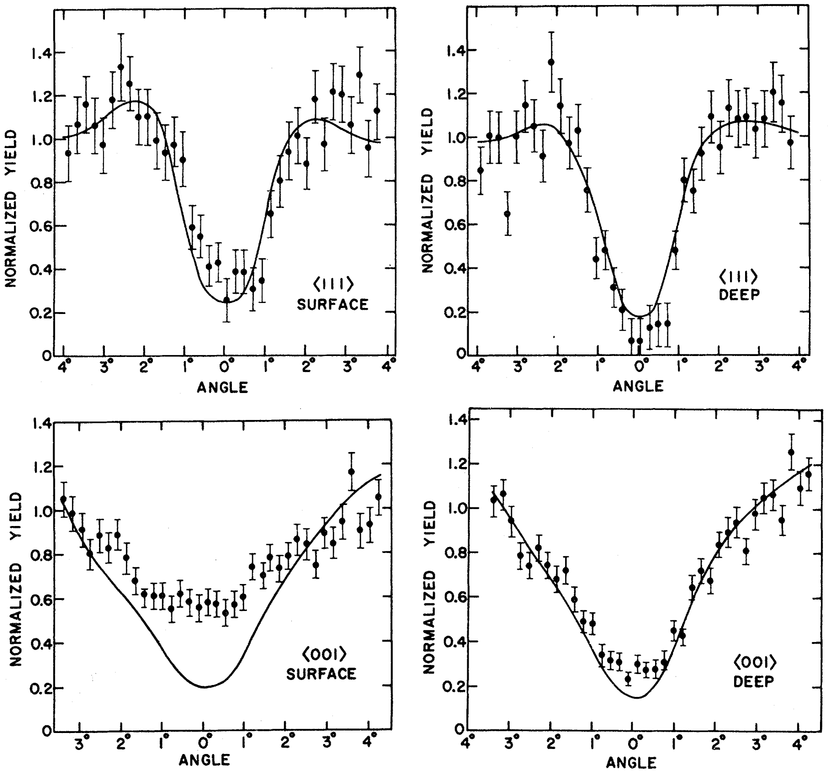

FIG. 2. Normalized backscattered yield as a function of tilt angle about the ⟨111⟩ and ⟨001⟩ axes. Solid lines are yields from Sn and data points are yields from Au. The words SURFACE and DEEP refer to the energy windows II and I, respectively, shown in Fig. 1.

determined to be 0.3 at.% at 209 °C, the temperature of the diffusion anneals.

Repeated scans of several crystalline planes revealed that there was no significant difference between the angular dependences of backscattered yield from Sn host atoms and Au impurity atoms. Detailed angular scans of the ⟨001⟩, ⟨100⟩, and ⟨111⟩ axes were also made, since such axial scans are expected to be more sensitive than planar scans to the precise position(s) of impurity atoms not located on lattice sites. Within the limits of the counting statistics for these measurements, the deep scans of Ne backscattered from Au and from Sn are the same. Figure 2 shows the detailed angular scans of the ⟨001⟩ and ⟨111⟩ axes for Sn and Au, both surface and deep. It is evident that the minimum yield for Au in the near-surface region of the crystal is significantly higher than that for Sn, especially in the ⟨001⟩ direction. Although it is not obvious, this might be a flux-peaking effect.

One sample, whose ⟨100⟩ axis was normal to the surface, was accidently raised to 225 °C for a short period, immediately after transfer to the channeling target chamber. The scan shown in Fig. 3 was measured at 217 °C shortly thereafter. The asymmetry of this scan strongly suggests that the concentration of Au within the first 600 Å of the sample was decreasing significantly during the measurement. Raising this sample above the eutectic temperature of 217 °C most likely caused melting to occur at the surface, since the Sn was nearly saturated in Au. The phase diagram[13] shows that at 225 °C such a sample will segregate into Au-enriched Sn liquid and Au-depleted Sn solid. Liquid will then form at the surface, as Au diffuses from the interior. After cooling the sample again to 217 °C, resolidification occurs concomitantly with diffusion of Au from the surface region back into the sample bulk. It is quite likely that the decrease of Au concentration near the surface, as evidenced by Fig. 3, is due to the rediffusion of Au back into the sample interior, following the partial melting just discussed. This accidental measurement may in fact be the first *in situ* "real-time" nondestructive measurement of impurity diffusion by ion-backscattering techniques. It is evident, then, that the channeling and backscattering techniques may be very useful for many other measurements of atomic mobility and chemical reactions in materials.

IV. DISCUSSION

Diffusion investigations[1-5] present convincing evidence that the noble metals diffuse interstitially in lead, tin, and other polyvalent hosts. There is even evidence that much more complex defects than simple interstitials are involved, such as in-

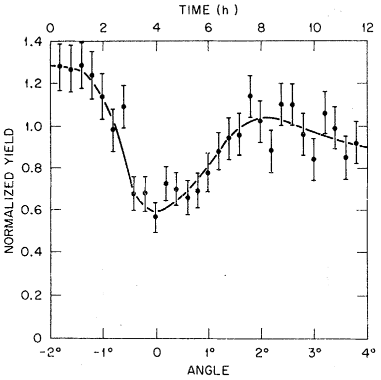

FIG. 3. Normalized backscattered yield as a function of tilt angle about the ⟨100⟩ axis, from the dissolved Au. Tho solid line is a smooth curve for the data shown. Reasons for the obvious asymmetry of these data are discussed in the text.

terstitial-vacancy close pairs[2,20] and diplons.[3] It has been suggested[1-3] that the dissociative mechanism of dissolution[6] is involved in these cases, and that equilibrium is maintained between substitutional impurity atoms, free interstitial atoms, interstitial-vacancy close pairs, diplons, and vacancies. Without some more direct measurement of these defect types, it has been virtually impossible to (i) show that the dissociative mechanism does indeed apply to these cases and (ii) determine the relative fractions of the several impurity defects involved. This channeling study provides some of these answers quantitatively.

Excepting the surface axial scan data for the moment, all other planar and axial scan data are the same for both Sn and Au, within the experimental error. From these data we estimate that 95% or more of the Au atoms dissolved in equilibrium conditions in Sn at 217 °C are substitutional. Considering this evidence together with that for the interstitial mechanism of diffusion, it is evident that the dissociative mechanism of dissolution is operative in this system, and most probably operative in all the other very similar systems, i.e., noble-metal impurities dissolved in polyvalent hosts. Of further interest, the ultrafast diffusion of Au in the Sn ⟨001⟩ direction is thus due to only the 5% or less of the dissolved Au atoms that are interstitial.

In considering the surface data for which minimum yields for Au are higher than for the host Sn, it is possible to rule out the possibility that layers of pure Au at the surface might give rise to this effect; a peak in the Au random spectrum at the surface would have been observed in this case. Given also the lack of any obvious flux-peaking effects, it seems unlikely that the Au atoms responsible for this increased backscattering yield near the surface are in unique symmetrical interstitial sites. Perhaps the ~25% of the Au atoms in this region are instead located in more random positions in the lattice. Since dislocation density might be much higher near the surface than in the bulk, Au atoms segregating to dislocations would be located at rather random positions in the lattice, and could give rise to the observed increase in minimum yields. The change in internal friction peaks[21,22] observed after further etching of Pb (Au) samples is evidence of similar near-surface behavior of Au in a polyvalent host and the studies of Rossolimo and Turnbull[23] demonstrate the tendency of gold to segregate to dislocations in such metals. Nevertheless, segregation of Au atoms to dislocations near the surface is considered unlikely as a complete explanation, since inordinately large dislocation densities would be required. The mechanism for this near-surface effect, although not well understood, may be a consequence of the ion beam not being in statistical equilibrium this close to the crystal surface.

It is possible that the great difference in diffusivities of Cu, Au, and Ag in polyvalent hosts is primarily due to the greater or lesser tendency of each impurity to dissolve interstitially. In this view, we should expect the interstitial fraction of dissolved Au, whose diffusivity is at least two orders of magnitude slower than Cu, the fastest diffuser, to be less than 1%. The consistency of our results with this expectation lends strong support to this interpretation of the relative diffusivities.

Our conclusion that the interstitial fraction of Au atoms in Sn is close to the limit of sensitivity of the measurements is in contrast to the results of Tomlinson and Howie[24] for Au in Pb, as determined by electron-blocking effects. The diffusional behavior and solubility of noble metals in these two hosts are so similar that one would expect close agreement. Let us first note that their study was accomplished at room temperature after quenching from equilibrium conditions, and that recent studies[23] show equilibrium defect fractions may not be frozen in by quenching this alloy. Furthermore, the Rutherford backscattering of channeled ions is better understood quantitatively than channeling and blocking effects for electrons. We therefore believe that our results, and the interpretation thereof, are on firmer ground.

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[†] Present address: Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830.

[‡] Permanent address: Université de Lyon, Lyon, France.

[§] Present address: Varian Associates, Park Ridge, Ill.

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