ty of one of the 11 Na electrons, one has a large background to subtract. We feel we have coped successfully with those difficulties but another independent quantitative measurement of Na would still be welcomed.

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Evidence of Two Simultaneous Mechanisms for Diffusion of Cu in Pb Single Crystals*

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The radioactive-tracer method and sectioning technique were used to measure the diffusion coefficient of Cu in Pb single crystals under hydrostatic pressures between 1.75 and 9.00 kbar, at temperatures between (206 ± 1) and (326 ± 1) °C. The diffusivity at 1.75 kbar is described by $D_{1.75} = 0.95 \times 10^{-2} e^{-8800/RT}$ cm^2/sec^{-1}, which is in good agreement with previoulsy published results; the diffusivity between 3 and 9 kbar is described by $D_{3 \text{ to } 9} = 6.18 \times 10^{-2} e^{-10\,900/RT}$ cm^2/sec^{-1}. Average activation volumes between $P = 0$ and 1.75 kbar are in the range of $0.7V$ (V is the atomic volume of Pb); above $P = 3.38$ kbar, they are nearly zero.

I. INTRODUCTION

Diffusion results were interpreted for many years on the basis of single mechanisms. Recent evidence, particularly from pressure-diffusion[1–5] and related[6] experiments pointed to the possible coexistence of more than one mechanism in certain single solvent–solute systems. The diffusion of noble metals in lead looks interesting seen in this context. Intermetallic diffusion in all other fcc solvents is attributed to a vacancy mechanism, but the low values of the activation energy Q for the diffusion of noble impurities in lead were interpreted[7–11] on the basis of interstitial mechanisms.

Van der Maesen and Brenkman[12] first proposed that copper dissolves both interstitially and substitutionally in germanium. Ascoli *et al.*, on the basis of pressure-diffusion results[3] and almost

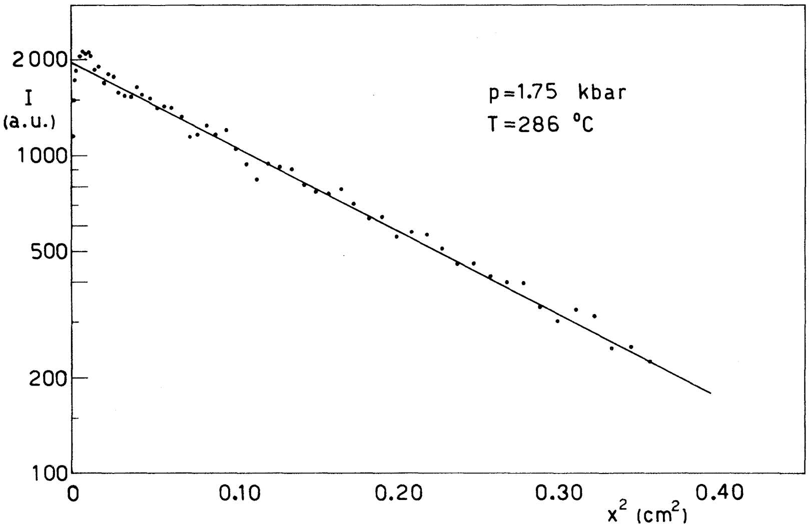

FIG. 1. Typical penetration plot: $P=1.75$ kbar, $T=286$ °C.

simultaneously Kidson,[13] proposed that the solution of gold in lead, too, can be both interstitial and substitutional, and that the diffusion of Au in Pb can take place through both vacancy and interstitial mechanisms. Turnbull and co-workers extended the proposal of interstitial and substitutional solution to other noble solutes[9–11] and polyvalent solvent metals, [14–17] but they added that diffusion in such systems should take place primarily through the interstitial mechanism. Subsequent experimental evidence supported this[18,19] or a somewhat refined[20] model for diffusion at zero applied pressure.

II. THEORETICAL CONSIDERATIONS

An equilibrium between solute configurations implies comparable activation energies of formation. Migration-energy values may then favor a diffusion mechanism based on one solution model rather than mechanisms based on other solution models. However, since the interaction potentials between solvent and solvent ion cores are generally different from those between solvent and solute ion cores, activation volumes ΔV are not necessarily higher for processes with higher activation energy Q, and vice versa. A process predominant at zero pressure may therefore be hindered at a higher hydrostatic pressure P, and then yield to a higher-energy process.

In fact, diffusion experiments of Au in Pb single crystals[3] under high hydrostatic pressure produced two different sets of values for Q and D_0 (the preexponential factor in the Arrhenius dependence of diffusion coefficient D on temperature T). One set holds for diffusion below a certain transition pressure P_t ($P_t \simeq 7$ kbar for Au diffusing in Pb), the other set holding above this pressure. This result was attributed to the fact that two mechanisms were simultaneously active in this system, i.e., a vacancy mechanism predominant below P_t, and an interstitial mechanism predominant above P_t. Results on Ag diffusing in Pb under pressure[2] were also interpreted on the basis of a vacancy plus an interstitial mechanism.

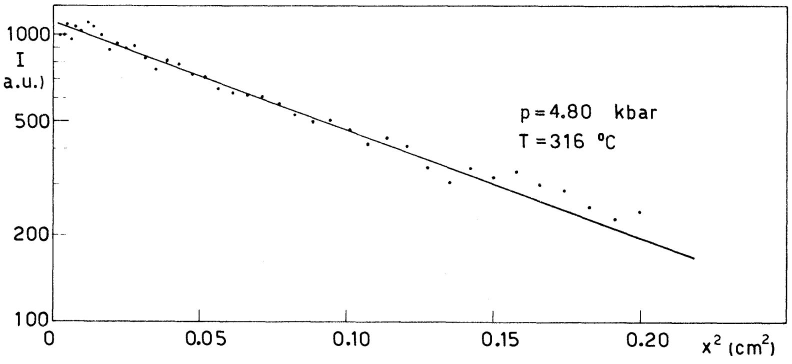

FIG. 2. Typical penetration plot: $P=4.80$ kbar, $T=316$ °C.

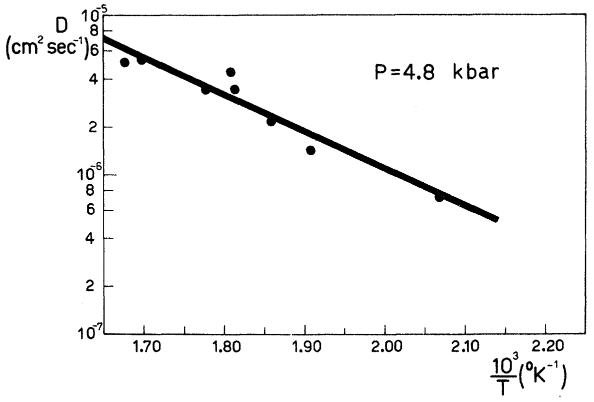

FIG. 3. Dependence of the measured diffusion coefficient D on temperature at $P = 4.80$ kbar.

III. EXPERIMENT

To check whether more than one mechanism would be responsible for the diffusion of another noble solute in lead, we performed a pressure-diffusion experiment of Cu in Pb single crystals. The apparatus and method used for the Au in Pb experiment[3] were adopted for the present work too, except that neutron-activated Cu was chemically deposited from a copper acetate solution on one flat surface of cylindrical 99.998% pure Pb single crystals, 1.1 cm in diameter, about 1 cm long. The thickness of the Cu deposit turned out to be some hundreds of atomic layers. Each sample was annealed for a time interval ranging from 1 h 16 min to 21 h 30 min, at a temperature between (206 ± 1) and (326 ± 1) °C, and at a fully hydrostatic pressure between 1.75 and 9.00 kbar. Diffusion annealings were performed at 5 to 8 different temperatures at each chosen value of pressure. After annealing, 100 to 120 slices (50 μ thick) were microtome cut from each sample, and annihilation quanta from positron decay of ^{64}Cu in the slices were detected by a scintibloc model No. 76S76 detector and analyzed by means of a 400-channel pulse-height analyzer.

IV. RESULTS AND CONCLUSION

Figures 1 and 2 show two typical penetration plots. The activity-vs-penetration data were least-squares adjusted for each of these plots, and the resulting diffusion coefficients D at each pressure were Arrhenius plotted. Figure 3 shows the Arrhenius plot at 4.80 kbar. The D-vs-T values at each P were also least-squares adjusted to give Q and D_0 values. First results at $P = 1.75$, 3.38, 4.80, 6.20, 7.50, and 9.00 kbar (Fig. 4) show Q-vs-P and D_0-vs-P dependences similar to those for Au in Pb, with P_t located between 2 and 3 kbar (below 2 kbar, $Q \simeq 8.5$ kcal/mole; above 3 kbar, $Q \simeq 10.9$ kcal/mole). The activation volume ΔV of the process for different temperatures, averaged over the low- as well as the high-pressure ranges, is given in Table I in units of V, the atomic volume of the solvent. It can be seen that at $P < P_t$, ΔV is a large positive fraction of V, whereas at $P > P_t$, $\Delta V \simeq 0$, as was found for Au diffusing in Pb.

TABLE I. Activation volume ΔV (in units of atomic volume V of the solvent) for the diffusion of Cu in Pb, averaged in the indicated pressure ranges.

Temperature (°C)	$\Delta V/V$ $0 < P < 1.75$ kbar	$\Delta V/V$ $3.38 < P < 9.00$ kbar
327	0.69	0.076
260	0.72	0.079
200	0.75	0.096

The same two-mechanism interpretation put forward for the Au in Pb results[3] could therefore explain the present results on Cu in Pb. Although evidence for interstitial diffusion at $P = 0$ seems by now to largely exceed[9,11,14–20] that for vacancy diffusion,[2,3,13] yet the only direct measurements of ΔV, namely, pressure-diffusion experiments, giving large positive values of ΔV at the lowest pressures, once again cast some doubt on diffusion models based exclusively on one interstitial mechanism.

After this work had been completed, a pressure-diffusion experiment of Cu in Pb up to 56 kbar was published by another group of workers,[21] but with no experimental points between 0 and 20 kbar. There is no overlapping with our measurements. These workers find $\Delta V = 0.04 \pm 0.03$, which gives a fair cross check with our results for $P > P_t$ (see last column of Table I). Their conclusion, that most of the diffusion of Cu in Pb takes place by an interstitial mechanism, is not inconsistent with the double-mechanism model proposed by us, since their conclusion is based on measurements at $P = 0$ or at $P > P_t$ and our model also foresees an

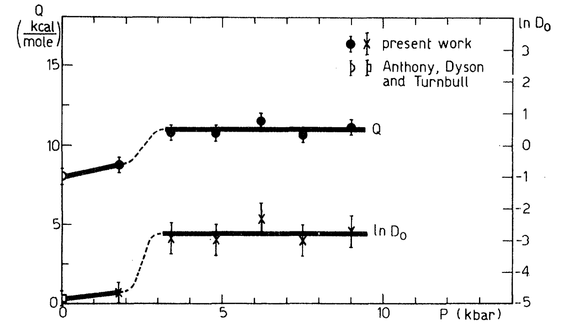

FIG. 4. Dependence of the activation energy Q and preexponential factor D_0 (as obtained from experimental graphs like that in Fig. 3) on the annealing pressure. Q and D_0 values at $P = 0$ are taken from Ref. 9.

interstitial mechanism in the high-pressure range and a vacancy mechanism only in the low-pressure range where a "fine-structure" search is lacking in Ref. 21.

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Low-Energy-Electron Diffraction from Several Surfaces of Aluminum

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A model for aluminum used previously for low-energy-electron-diffraction (LEED) calculations by the layer Korringa–Kohn–Rostoker method on the {001} surfaces, is carefully defined and used to find LEED spectra for the {111} and {110} surfaces. Agreement between theory and experiment is as good for {111} as for {001}, but is not as good for {110}, which appears generally to be a "bad actor." Close comparison of the shapes of lines in the experimental and theoretical spectra suggests values for the interlayer spacing of the outermost layer of the crystal which are roughly 5% greater than bulk for the {111} face but 10% less than bulk for the {110} face.

I. INTRODUCTION

A model for aluminum and method of calculation for low-energy-electron diffraction (LEED) has been described by us previously[1,2] with detailed application to Al{001}. This work gave satisfactory agreement with experimental LEED spectra (i.e., flux density in diffracted beams versus energy at fixed angles of incidence) on the {001} surfaces for energies up to 150 eV for several beams and for a range of incident polar angles (i.e., angles with the surface normal) from 0° to 25°. In the present paper, we apply the same model and calculation procedure to the {111} and {110} surfaces of Al and compare the results for all surfaces. We also take the opportunity to describe the model care-