where ΔV_{is} and ΔV_{ps} are the derivatives of I and Q with respect to pressure, and the other energies and volumes correspond to pure substitutional, interstitial, and pair diffusion according to the subscripts.

Assuming that the diffusion of these tracers in lead is characterized primarily by the equilibrium fractions p and q, one can from the present data, estimate the p's and q's for each as well as the parameters D_i, ΔH_i, ΔV_i, ΔV_{is}, D_p, ΔH_p, ΔV_p, and ΔV_{ps}. The remaining parameters D_s, ΔH_s, and ΔV_s were chosen to correspond to the respective values measured for self-diffusion. The assignment is justified by the fact that the charge of those atoms is likely completely screened in polyvalent lead at the nearest neighbor distance.[31] The measured values of D, ΔH, and ΔV, for the eight tracer experiments, all evaluated at atmospheric pressure and 600 K, coupled with Eqs. (3), (5), and (6), gave 24 nonlinear equations in 24 unknowns. These were algebraically reduced to eight equations with eight unknowns and then solved by computer using a nonlinear least-squares-fitting technique[32] to yield the results in Table III. Although the assumption that the diffusion parameters are independent of the diffusing impurity may be questioned, the p's and q's, along with the corresponding energies I and Q, seem very reasonable and are close to what one might have expected. The results indicate that Cu dissolves almost entirely as an interstitial impurity, whereas Au and Ag have a decreasing interstitial fraction. Palladium and Ni have larger pair fractions than interstitial, whereas Cd and Hg form primarily substitutional alloys with less than 1% contribution from pairs or interstitials.

In calculating the isotope effect for this model, we realized that there must be a mass dependence for the D_s, D_i, and D_p in Eq. (3), so we included such an effect and repeated the least-squares fitting. The results were not substantially different from those given in Table III, except for the case of Cu, where q dropped from 0.98 to 0.7 and p increased to 0.3. The isotope calculations yielded values that were much too large,[8,9,33] unless we assumed the isotope effect for the interstitial motion to be $\simeq 0.25$. This would indicate a correlated motion of several atoms in the interstitial jump.

The parameters in Table III, when used with Eqs. (3), (5), and (6), yield $D(0, 600\,^{\circ}\mathrm{K})$ to within ±3%, $\Delta V/V_0$ to within ±0.02, and gave values of ΔH to within ±8% of the measured values. It is also interesting to note that in spite of the fact that Eq. (3) involves the sum of three different exponential factors (D_s, D_i, and D_p), a plot of the theoretical values of $\ln D$ versus $1/T$ is linear to within a few percent for all the materials reported in this work over the temperature range of the measurements. Part of the reason for this might be due to the temperature dependence of the p's and q's, which is shown explicitly in Eq. (4), or to the dominance of the interstitial term in the diffusion rate of these materials.

TABLE III. Parameters for the substitutional, interstitial, and interstitial-vacancy-pair dissociative mechanism determined from diffusion measurements of eight impurities in lead and the equilibrium fractions of interstitial, q, and pair type p defects for these impurities. The energies Q and I are calculated from Eqs. (4).

Impurity	p	q	Q (eV)	I (eV)
Cu	0.01	0.98	0.08	−0.22
Pd	0.54	0.28	0.04	−0.02
Au	0.05	0.18	0.21	0.07
Ni	0.65	0.11	0.04	0.04
Zn	0.45	0.10	0.09	0.08
Ag	0.06	0.024	0.23	0.19
Cd	0.0003	0.0008	0.52	0.37
Hg	0.002	0.0004	0.40	0.40

$D_i/D_s = 20\,660 \pm 40$ $\quad D_p/D_s = 1300 \pm 100$
$\Delta H_i = 0.354 \pm 0.001$ eV $\quad \Delta H_p = 0.90 \pm 0.06$ eV
$\Delta V_i/V_0 = 0.165 \pm 0.005$ $\quad \Delta V_p/V_0 = 0.65 \pm 0.10$
$\Delta V_{is}/V_0 = 0.110 \pm 0.005$ $\quad \Delta V_{ps}/V_0 = 0.57 \pm 0.03$

Although the analysis has been done for substitutional, interstitial, and pair-type defects, the theory, with very little change, would accommodate other types of defects. For example, the impurity-impurity and impurity-host diplons as proposed by Warburton[34] could be used equally well with only minor changes. These changes would involve merely a redefinition of Q and I and would replace the 6 in Eq. (3) with a different number because of different probabilities in the distributions.

We conclude that the diffusion of Pd in Pb is very rapid and is nearly independent of pressure, but that it takes place by a mechanism which is quite different than that of copper, which appears to be essentially by free interstitials. This diffusion of Pd in Pb can be explained in terms of a large contribution from interstitial-vacancy pairs with some free interstitials. In this feature, it is quite similar to the diffusion of Ni in Pb. It would help to have enhancement experiments on the diffusion of Pb in a Pb(Pd) alloy, for we would expect a very different result for pair diffusion, which is enhanced similar to a direct interchange mechanism, and interstitial diffusion, which should show little if any enhancement. The most puzzling thing is the small activation volume which is considerably smaller than that for free interstitial or pair diffusion alone. Apparently, some of the major

terms in Eq. (6) must be of opposite sign, and cancel to give this result. Under these circumstances, it surely could not be interpreted in the usual way as an activation volume of some particular mechanism. This analysis may be too naive in letting D_i, D_s, and D_p be independent of the impurity. This is justified only for D_s.

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