reduces the rate at which positrons annihilate with the 4f electron to the point that a change in the 4f state cannot be observed by the angular-correlation method.

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Interstitial Diffusion of Copper in Lead at Pressures up to 56 kbar*†

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The diffusion of copper in lead has been investigated using radioactive-tracer and sectioning techniques. The measured diffusion coefficients span the hydrostatic pressure range 0–56 kbar and temperature range 218–530 °C. The activation energy and volume at the melting temperature and atmospheric pressure are, respectively, $\Delta H = 5.6 \pm 0.5$ kcal/mole and $\Delta V/V_0 = 0.04 \pm 0.03$. The pressure and temperature coefficients of the activation volume, although quite uncertain, were also determined. The small activation energy and volume indicate that copper diffuses in lead primarily by the interstitial mechanism.

I. INTRODUCTION

Recently there has been renewed interest in the relatively rapid diffusion of the noble metals in lead. A number of models have been proposed to explain this rapid migration of atoms, but more experimental data are needed to determine which, if any, of these models is correct. This work completes a set of high-pressure studies of the noble metals in lead. These metals, gold, silver, and copper, are very similar in electronic structure. Each is characterized by an inert-gas electron core in addition to a filled d shell and one s electron. The differences in their diffusivities in lead may be attributed primarily to size effects and to minor differences in binding.

Interestingly, one of the first reported investigations of solid-state diffusion involved the diffusion of the noble metal gold in lead. Roberts-Austen[1] found that gold atoms migrate rapidly in lead even at temperatures as low as 200 °C. Hevesy[2] measured lead self-diffusion and found that it was orders of magnitude slower than the diffusion of gold in lead. Seith and co-workers[3-5] measured the diffusion of a number of metals in lead. They found that the diffusion coefficients for silver and gold in lead were up to four orders of magnitude greater than for the other solutes. If gold and silver diffuse in lead by the vacancy-diffusion mechanism, a significant enhancement of lead self-diffusion would be expected in Pb-Ag and Pb-Au alloys. Measurements by Seith and Keil[6] showed that the expected enhancement of lead self-diffusion did not occur when gold impurity was added to the lead. Seith and Keil concluded that gold diffused in lead by the interstitial mechanism. This conclusion was contrary to the general experience that metallic alloys are substitutional solutions. Prior to Seith and Keil's publication, Hägg[7] proposed that no element would dissolve interstitially in another element unless the ratio of the diameters of the solute atom to the solvent atom were 0.59 or less. According to this rule, no metal would be expected to dissolve interstitially in any other metal except possibly the alkalies.

Interest in the diffusion of the noble metals in lead was rekindled with the discovery of the high mobility of atoms along grain boundaries and dislocations. Nowick[8] suggested that because of the low solubility of gold and silver in lead, all the diffusion could be along internal surfaces. However, Ascoli[9] proved that the diffusion of gold in lead was virtually unaffected by the density of grain boundaries. Kidson[10] showed that dislocations were not responsible for the rapid diffusion of gold in lead, and Dyson, Anthony, and Turnbull[11] found no difference in the diffusion of copper in polycrystals or single crystals of lead. Curtin, Decker, and Vanfleet[12] measured the activation volume for silver diffusion in lead via high-pressure techniques. This activation volume (as corrected by Weyland, Decker, and Vanfleet[13]) is 0.34 atomic volumes. This value is significantly larger than typical activation volumes for interstitial diffusion, but significantly smaller than typical activation volumes for substitutional diffusion. To explain this result, Curtin *et al.* proposed that silver diffused in lead by both the subtitutional and the interstitial mechanisms. Later Kidson suggested that Frank and Turnbull's[14] interstitial-substitutional dissociative model could be used to describe the diffusion of gold in lead.

High-pressure studies of the diffusion of gold in lead by Weyland *et al.*[13] showed that the activation volume, 0.28 atomic volumes, was very near the value obtained by Curtin *et al.* for silver diffusion in lead. The intermediate magnitude of the value seemed to support the double-diffusion-mechanism proposal.

The diffusion of copper in lead at atmospheric pressure was studied by Dyson, Anthony, and Turnbull[11] and was found to be even more rapid than the diffusion of silver or gold in lead. To complete the high-pressure analysis of the diffusion of the noble metals in lead, the diffusion of copper into lead has been examined at pressures up to 56 kbar in the temperature range 218–530 °C.

II. METHOD OF ANALYSIS

The analysis of diffusion as a function of temperature and pressure has generally been interpreted in terms of the activated-state theory of absolute reaction rates.[15] If we assume that there is a single diffusion mechanism, this theory leads to an expression for the diffusion coefficient D of the form

$$D(P, T)=fa^2\nu(P, T)\,e^{-\Delta G(P,T)/RT} \quad , \tag{1}$$

where f is the product of a geometric and correlation factor, a is the lattice parameter (a constant for the experiment because all samples are sectioned at about 23 °C and atmospheric pressure), ν is the mean vibrational frequency of the diffusing atoms, ΔG is the Gibbs free energy of activation per mole of activated complexes, R is the molar gas constant, P is the pressure, and T is the temperature. As discussed by Weyland *et al.*,[13] $\ln\nu(P, T)$ and $\Delta G(P, T)$ were expanded in Taylor's series about $P=0$ and $T=T_0$ and the coefficients in the expansions determined by a least-squares fit of the calculated $\ln D(P, T)$ to the diffusion data. In this manner one evaluates the preexponential factor

$$D_0=fa^2\nu(0, T_0)\,e^{\Delta S(0,T_0)/R} \quad , \tag{2}$$

the activation volume $\Delta V(0, T_0)$, the activation energy or enthalpy $\Delta H(0, T_0)$, and the temperature and pressure derivatives of the activation volume. The value of the specific heat of activation, as defined by Weyland *et al.*, was set equal to zero for the same reasons they gave.

III. EXPERIMENTAL PROCEDURE

Lead single crystals 3.6 mm in diameter were grown by the Bridgman technique in a vacuum of 10^{-5} Torr. The crystals were grown from 99.9999%-pure lead (obtained from Leico Ind.) in spectroscopic high-purity graphite molds. The lead crystals were sectioned into small right-circular cylinders 4 mm long. The surfaces of these cylinders were allowed to oxidize in the atmosphere for a day or more before being coated with tygon paint.

A clean lead surface was obtained, prior to plating, by slicing the lead crystal perpendicular to the cylindrical axis with a microtome. The clean lead surface was immediately etched in dilute nitric acid and transferred to an acidified radioactive-copper nitrate solution where Cu^{64} was chemideposited on the bare lead surface. After plating, the lead cylinder was rinsed in a series of methyl alcohol and acetone baths and blotted dry. The cylindrical surface was machined off to remove copper which might have penetrated the tygon paint or lead oxide.

Curvature of the concentration profiles of our first samples indicated that there was some oxidation holdup at the plated surface. To eliminate this effect, the following "preanneal" procedure was used. After machining the cylindrical surface, the lead crystal was dipped into hot silicone fluid (about 310 °C) for about 12 sec so that some of the radioactive copper would diffuse a short distance into the crystal. A 4-μ slice was then taken from the plated end of the crystal to remove the radioactive copper which had not dissolved into the lead during the preanneal. Eight samples were sectioned and counted immediately after the preanneal procedure so that a correction could be made for the diffusion that occurred during the preanneal. The crystals were about 3.1 mm in diameter and 2.8 mm long after sample preparation was completed.

Following the preanneal each crystal was then placed in a pressure cell similar to the one described by Curtin, Decker, and Vanfleet.[12] The major differences were that we used petroleum ether (bp 110–115 °C) for our hydrostatic pressure medium, Inconel for the heater can, and 0.025-mm polyimide film liner to electrically insulate the sample from the Inconel can. The ram load of the tetrahedral press was raised to the desired level and the sample was then heated electrically. Two Kepco KS-100 power supplies supplied up to 270 W to the Inconel heater. The temperature of the sample was monitored with a chromel-alumel thermocouple which was connected to a Moseley x-y recorder. Temperatures were held constant to within ± 1 °C during the time of anneal. Temperature rise and fall times were less than 40 and 15 sec, respectively, and never exceeded 15% of the total anneal time. After completing each high-pressure anneal it was necessary to lower the ram load slowly in order to avoid pressure-cell blowouts. Periods as long as 1 h were required to bring the sample down to atmospheric pressure safely.

The lead crystal was then removed from the pressure cell and the cylindrical surface was machined to the final diameter of about 2.8 mm. The sample was then embedded in paraffin wax to prevent plastic smearing of the crystal surface while sectioning with the microtome. Each crystal was cut into 20-μ slices perpendicular to the cylindrical axis. The slices were counted in groups of ten. The activity of each 200-μ section was measured with a Tracerlab well-counter and a RIDL multichannel analyzer. The gates for the multichannel analyzer were set so that only γ rays with energies in the region of the 0.51-Mev peak were measured.

A. Pressure Calibration

High-pressure calibration in the tetrahedral press at elevated temperatures in the range of this experiment was difficult because of the lack of calibrants and available techniques. We have calibrated our hydrostatic cell at room temperature, however, by correlating both the hydraulic ram load and the electrical resistance change of a manganin coil at the phase transformations of the calibrants, Hg L-I, Bi I-II, Tl II-III, and Ba I-II. The up-cycle pressures for these phase transformations were taken to be 12.0,[16] 25.8, 38.0, and 56.0[17] kbar, respectively. The problem arises in that having applied a given ram load, corresponding to a pressure P_0, the pressure changes quite significantly at the sample for temperature changes of only 100–200 °C.[18,19] We have estimated the resultant pressure changes in the hydrostatic cell for temperature changes ΔT in the range 0–175 °C by measuring the resistance change of a manganin coil. Pressures along the room-temperature isotherm are commonly determined from the fractional change in resistance $r(P, 0)$ of a manganin coil using the equation

$$P = Ar(P, 0) + Br^2(P, 0) \quad , \tag{3}$$

where the constants A and B are determined by measuring the manganin-resistance changes for the above calibration points. Wang[20] has investigated the change in electrical resistance of manganin as a function of temperature along various isobars up to 4 kbar. According to his results, $r(P, \Delta T)$ along any isobar is given by

$$r(P, \Delta T) = r(P, 0) + r(0, \Delta T) + CP\Delta T \quad , \tag{4}$$

where $CP\Delta T$ is a small correction term ($C = 4.4 \times 10^{-7}$/kbar °C), and $r(P, \Delta T)$ is the fractional change in manganin resistance at pressure P and temperature change ΔT. The fractional manganin-resistance change $r(0, \Delta T)$ was measured outside the pressure cell and $r(P, \Delta T)$ was measured in the press at seven different ram loads and eight different temperatures ranging from 15–45 kbar and 25–200 °C. The pressure P was then calculated by solving for $r(P, 0)$ from Eq. (4) and substituting it into Eq. (3). The change in pressure ΔP due to heating is the difference P-P_0 measured at constant ram load. The values of ΔP were found to be independent of the ram load within the experimental accuracy of the measurements. The averaged data are shown in Fig. 1 along with a best-fit empirical curve of the form

$$P = a\Delta T^b(1 - e^{-c\Delta T^d}) \quad . \tag{5}$$

The constants $a, b, c,$ and d were determined by a least-squares fit of the experimental points. The

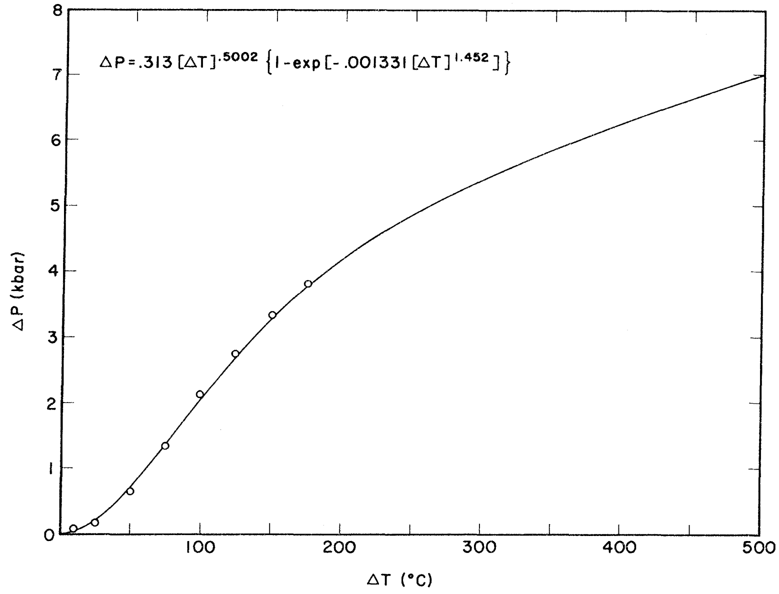

FIG. 1. Pressure increase in the hydrostatic cell as a function of temperature change above room temperature for constant hydraulic ram load.

extrapolation formula, Eq. (5), was chosen because it has the essential features of a curve through the experimental points and extrapolates smoothly without oscillating.

There are several problems associated with our measurements of ΔP which should be pointed out. First, we have no assurance that Eq. (4) is valid for pressures above 4 kbar. If, for example, the coefficient C were zero, ΔP would increase by as much as 20%. A second difficulty is that we were not able to make manganin-resistance measurements in the actual temperature range of our diffusion anneals (218–530 °C). This was because the curve $r(0, \Delta T)$ shifted if the manganin coil was heated above 220 °C during any temperature cycle. Therefore, it was necessary to extrapolate our measurements of ΔP into the temperature range of our diffusion anneals. It should be pointed out that, when Curtin *et al.*[12] measured the diffusion of silver in lead at this laboratory, they did not make a pressure correction for temperature. When their data were corrected by the amounts we have calculated, their activation volume came into good agreement with the measurements of Gilder.[21] The activation energy, which already agreed with the results of Dyson *et al.*[11] was virtually unaffected.

B. Corrections and Errors

Several corrections were made in the data in order to arrive at the reported diffusion coefficients and parameters. First, the count rate for every sample section was corrected for background and radioactive decay. The latter was necessary because of the short, 12.8 h, half-life of the Cu^{64} isotope which was used.

Second, the anneal time for each sample was corrected for heat up, cool down, plus all time that the sample spent at room temperature. The corrections to the anneal time, which involve a knowledge of $D(P, T)$, were made by an iterative technique and were found never to exceed 6% of the total anneal time.

The error assigned to our measured values of the diffusion parameters includes the standard deviation, calculated by the usual techniques, plus errors that would be caused by estimated maximum-possible systematic errors in temperature and pressure. For example, Getting and Kennedy[22] disagree with Hanneman, Strong, and Bundy[23] by as much as 6 °C on the amounts by which chromel-alumel thermocouples should be corrected for pressure in the range of this experiment. One set of diffusion parameters was calculated using Getting and Kennedy's correction, and a second set was calculated using Hanneman, Strong, and Bundy's correction. The difference between the values for each diffusion parameter obtained from the two calculations was combined with the standard deviation for that parameter. A similar procedure was used in conjunction with the pressure calibration. A second set of parameters was calculated using an estimated worst-possible pressure calibration, obtained by using $\frac{1}{2}\Delta P$ and by lowering the room-temperature calibration by one standard deviation. Here again the difference between the two values for each parameter was combined with its standard deviation.

IV. RESULTS

The concentration profiles for three samples are shown in Fig. 2. Profile B is typical of our first diffusion attempts where marked curvature

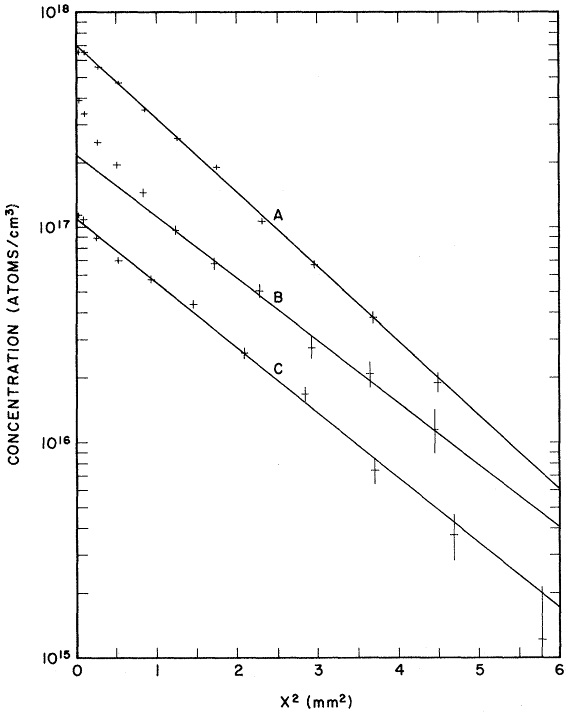

FIG. 2. Solute concentration profiles of Cu in Pb for three samples. The sample represented by curve A was preannealed, then annealed at 412 °C at 21 kbar for 371 sec. The sample represented by curve B was annealed at 238°C and atmospheric pressure for 1200 sec. The sample represented by C was preannealed, then annealed at 280 °C and atmospheric pressure for 660 sec.

was observed near the plated surface. Similar curvature has been reported by other experimenters[11,24] in cases where the diffusion of some of the tracer has been retarded at the plated surface by oxide layers. To test this possibility we initiated our preanneal technique which consists of (a) annealing the sample briefly immediately after plating and (b) slicing a thin layer from the plated surface to remove any copper which had not already dissolved in the lead. Concentration profiles A and C are typical of the samples that were first prepared by this preanneal procedure and then annealed at the desired temperature and pressure. All of the concentration profiles obtained from preannealed samples appeared to be Gaussian over the 1–2 decades of concentration range that we were able to obtain experimentally.

Eight samples were sectioned immediately after the preanneal. The copper concentration in the first 20-μ section (not including the 4-μ section that was cut off to remove undissolved copper) was typically 100 times greater than the concentration in the second 20-μ section. The effective anneal time for the preanneal was less than 1% of the total diffusion anneal time. From these results we felt justified in approximating the concentration of copper in lead after the preanneal by a δ-function source.

The counting procedure for three of the samples was altered in order to determine the concentration profile near the plated surface. For these samples the first 10 slices were counted individually. In each case the first 20-μ slice contained an excessive concentration of copper while the second, third, and fourth slices formed an inverted slope in the concentration profile. Evidently, some copper precipitates out to the surface between the end of the high-temperature diffusion anneal and the time the sample is sectioned. Barr, Mundy, and Smith[25] examined this effect for the diffusion of gold in sodium.

The $\log_{10}$ of the diffusion coefficients as a function of pressure is shown in Fig. 3 for the diffusion of Cu in Pb for the 600 and 700 °K isotherm. However, because no two samples were annealed at exactly the same temperature, small temperature corrections, using the expansion of Eq. (1), were made in order to shift the data points to the ap-

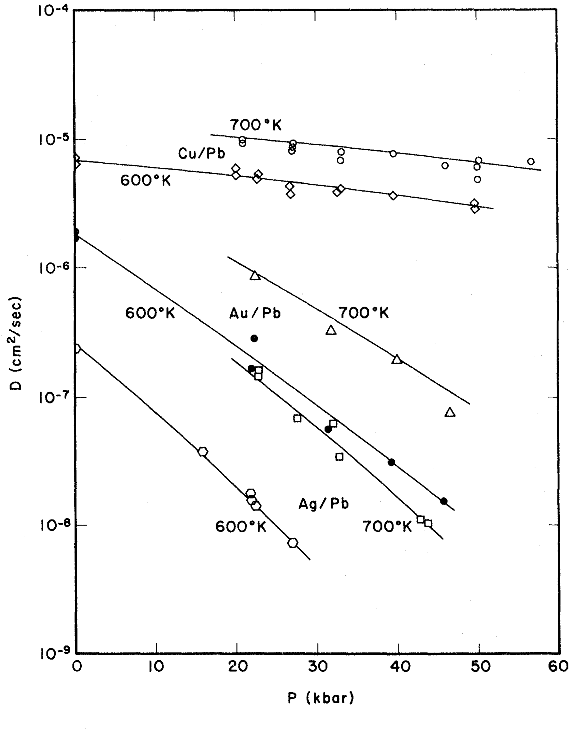

FIG. 3. Variation of the diffusion coefficient with pressure at constant temperature. The zero-pressure data for Au and Ag in Pb are from Refs. 10 and 6, respectively. The high-pressure data for Au and Ag in Pb are from Ref. 13. The solid curves are the best fit of the data to Eq. (1). ○ —measured diffusion coefficients for Cu in Pb at 700 °K; ◇ —Cu in Pb at 600 °K; △ —Au in Pb at 700 °K; ● —Au in Pb at 600 °K; □—Ag in Pb at 700 °K; ○ —Ag in Pb at 600 °K.

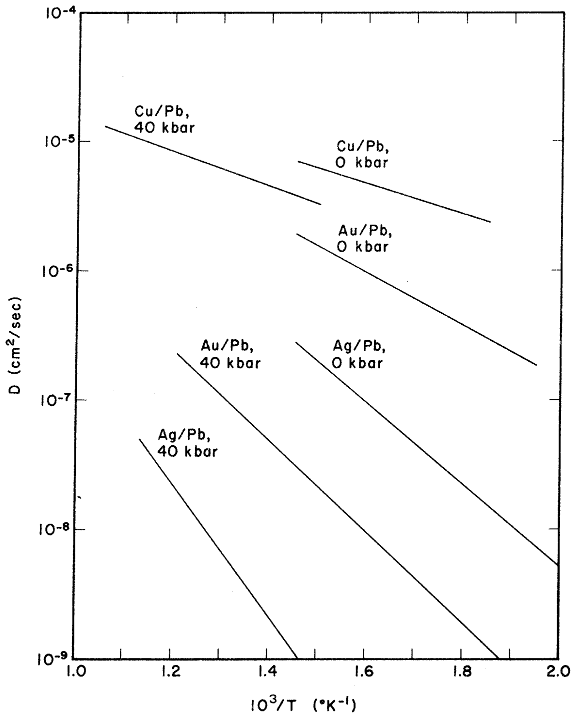

FIG. 4. Variation of the diffusion coefficient with inverse temperature at constant pressure. The curves were obtained from the best fit of all data to Eq. (1). The data for Au and Ag in Pb are from Ref. 13.

propriate isotherm. The solid lines are the best-fit curves of all the data from Eq. (1) and show how well the data fit the theoretical model. The $\log_{10}$ of the diffusion coefficient vs $1/T$ for the diffusion of Cu in Pb is shown in Fig. 4 for the 0- and 40-kbar isobar. Because no two data points occur at the same pressure, only the best-fit curves from Eq. (1) are shown. The $\log_{10}$ of the diffusion coefficient vs the reduced temperature $T_m(P)/T$ is shown in Fig. 5 for comparison with Nachtrieb's[26] postulated law of corresponding states for the diffusion of Cu in Pb. $T_m(P)$ is the melting temperature of lead[27] at the pressure P. The activation energy as a function of pressure for the diffusion of Cu in Pb is shown in Fig. 6. For comparison, corresponding data for the diffusion of Ag and Au in Pb reported by other investigators have been included where available and appropriate in Figs. 3–6.

Table I displays the experimental values for the preexponential factor D_0, the activation energy ΔH, the activation volume per atomic volume $\Delta V/V_0$, and the pressure and temperature coefficients of the activation volume for the diffusion of the noble metals in lead along with corresponding values of other investigators.

V. DISCUSSION AND CONCLUSIONS

High-pressure studies of materials known to diffuse by the vacancy mechanism have shown that, in almost every case, the activation volume is between 0.5 and 1.0 atomic volumes. Conversely, activation volumes for materials known to diffuse by the interstitial mechanism are much closer to zero (0.2 atomic volumes or less). Theoretical calculations are in agreement with these results.[28,29] The activation volumes for Ag in Pb, 0.34 atomic volumes, and for Au in Pb, 0.28 atomic volumes, seem to be too small for vacancy diffusion, yet too large for interstitial diffusion. In contrast, the activation volume for Cu in Pb, 0.04 atomic volumes, definitely lies in the range characteristic of pure interstitial diffusion.

Weiser[30] has pointed out that one evidence that an impurity diffuses by the interstitial mechanism is that its activation energy is significantly smaller than the activation energies for materials which are known to diffuse substitutionally in the same solvent. Tin, thallium, mercury, and bismuth are believed to diffuse substitutionally in lead. The

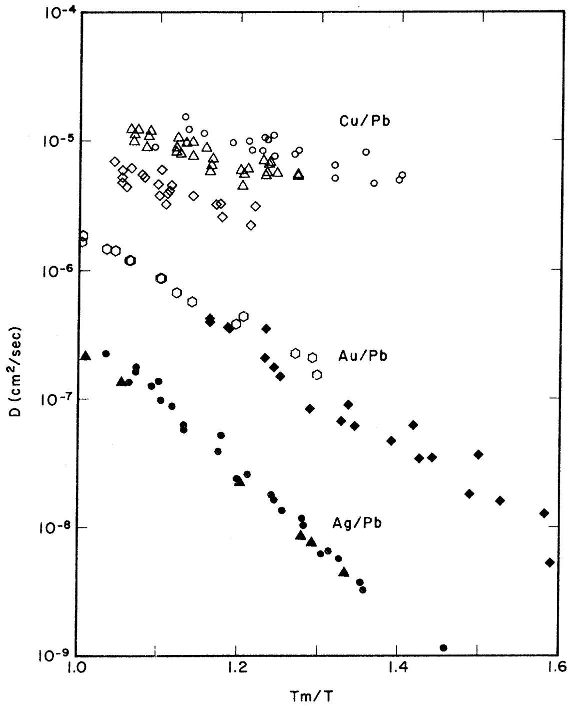

FIG. 5. Variation of the diffusion coefficient as a function of the ratio of the melting temperature to the annealing temperature. The data for Cu in Pb: ◇—atmospheric pressure; △—19–35 kbar; ○—38–56 kbar. The data for Au in Pb: ○—atmospheric pressure (Ref. 10); ◆—22–47 kbar (Ref. 13). The data for Ag in Pb: ▲—atmospheric pressure (Ref. 6); ●—15–44 kbar (Ref. 13).

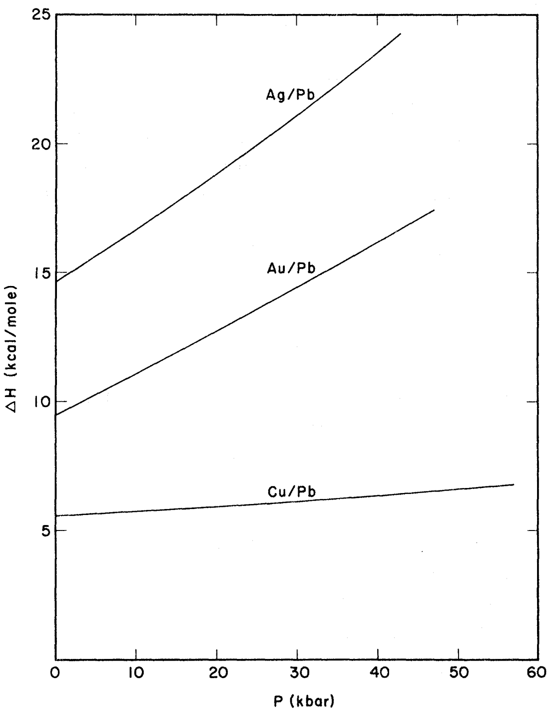

FIG. 6. Variation of the activation energy ΔH with pressure for Cu in Pb, Au in Pb (Ref. 13), and Ag in Pb (Ref. 13).

corresponding activation energies are 23.8, 20.9, 19, and 18.5 kcal/mole, as shown in Table I. These values are close to the activation energy for lead self-diffusion, 24.2 kcal/mole. The activation energies for Ag, Au, and Cu in lead are 14.6, 9.5, and 5.6 kcal/mole, respectively. These activation energies are smaller than the activation energies for impurities that dissolve substitutionally in lead. Notice, however, that the activation energy for Ag in Pb is closer to some of the activation energies for substitutional diffusion in lead than to the activation energy for Cu in Pb. This is another evidence that Ag in Pb does not seem to fit in either the substitutional or interstitial category. To explain their results for Ag in Pb, Curtin *et al.* proposed that the silver atoms diffuse by both the interstitial and vacancy mechanisms.

In support of this "double mechanism" proposal, Anthony[31] cited evidence from solution-hardening experiments that silver and gold dissolve in lead in both substitutional and interstitial positions. According to Westbrook and Aust's[32] results, silver causes solution hardening of lead approximately 50 times greater per at.% than any known substitutional solute in lead. They also found that gold was at least twice as effective in hardening lead as silver. Anthony assumed that interstitial impurities cause a greater increase in the local elastic distortion than can be caused by substitutional impurities. Thus he explained the solution hardening results by proposing that significant fractions of both gold and silver impurities dissolve interstitially and that this fraction is greater for gold than for silver. If this were true, one would expect Cu impurities to be even more effective in hardening lead.

This explanation is consistent with the diffusion results. Interstitial diffusion is characterized by smaller activation volumes and activation energies than substitutional diffusion. If Anthony's assumptions are correct, ΔH and ΔV for Ag and Au in Pb would be expected to be smaller than the corresponding quantities for impurities that dissolve substitutionally in lead. In addition, ΔH and ΔV for Au in Pb would be expected to be smaller than for Ag in Pb. The even smaller activation volume and activation energy for Cu in Pb can be explained if we assume that most of the copper atoms dissolve interstitially and diffuse by the interstitial mechanism.

To theoretically justify interstitial diffusion of the noble metals in lead, Anthony and Turnbull[33] point out that there is an unusually strong van der Waals binding between the ionic cores in the pure noble metals. Since lead has the same ionic core as gold, one might expect the same van der Waals attraction between the lead and noble-metal impurity ions provided the separation between ions is typical of the pure noble metals. The nearest-neighbor separations in pure Cu, Au, and Ag are 2.56, 2.88, and 2.88 Å,[34] respectively, while the distance between the center of the octehedral interstice and the nearest-lead lattice site is 2.48 Å,[34] which corresponds very well. Furthermore, since the noble metals are electronically very similar one might expect the ionic size of these impurities to be important in determining the differences in the mechanisms of diffusion. The ionic radii of Au^+ and Ag^+ are 1.37 and 1.26 Å, respectively, whereas Cu^+ is 0.96 Å.[34] This suggests a much higher probability of interstitial diffusion for Cu in Pb compared to Au and Ag in Pb.

The discrepancy in the activation energy for Cu in Pb as measured in this experiment, 5.6 ± 0.5 kcal/mole, and that measured by Dyson *et al.*,[11] 8.0 ± 0.4 kcal/mole, is well beyond the quoted uncertainties. There are several things aside from the difficulty of the experiment that should be considered. For instance, Peterson and Rothman[35] have noted that a number of erroneously high values of diffusion activation energies have been published by experimenters who have not completely eliminated the effects of oxidation holdup. Such a problem is likely to occur whenever tracer is plated in an aqueous solution.

TABLE I. Parameters for diffusion in lead.

Solute	D_0 (cm^2/sec)	ΔH (kcal/mole)	$\Delta V/V_0$	$\frac{1}{V_0}\left(\frac{\partial \Delta V}{\partial P}\right)_T$ (10^{-3}/kbar)	$\frac{1}{V_0}\left(\frac{\partial \Delta V}{\partial T}\right)_P$ (10^{-4}/°K)
Cu[a]	0.0008 ± 0.0006	5.6 ± 0.5	0.04 ± 0.03	0.5 ± 0.4	0.3 ± 0.4
Cu[b]	0.0079 ± 0.002	8.0 ± 0.4			
Au[c]	0.0052 ± 0.0015	9.5 ± 0.3	0.28 ± 0.03	1.0 ± 0.5	−1.4 ± 0.4
Au[d]	0.0025 to 0.0041	8.73 to 9.35	0.46		
Au[e]	0.0087	10.0			
Ag[f]	0.055 ± 0.013	14.6 ± 0.24	0.34 ± 0.04	3.0 ± 0.5	−1.9 ± 0.4
Ag[b]	0.046 ± 0.01	14.4 ± 0.5			
Ag[g,h]	0.074	15.2			
Pb[i]	0.46	24.8	0.64		
Pb[j]	0.281 to 1.37	24.2–26.1	0.72		
Pb[k]	1.17	25.7			
Bi[h]		18.5			
Hg[l]		19.0			
Tl[b]		20.9			
Sn[h]		23.8			

[a] This work. Parameters evaluated at 600 °K and atmospheric pressure.

[b] Reference 11.

[c] Reference 13. Parameters evaluated at 600 °K and atmospheric pressure.

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Dyson *et al.* seemed to have solved the oxidation holdup problem in spite of the use of an aqueous plating solution. Their example concentration profile, however, shows only one order of magnitude drop. Peterson and Rothman note that a concentration profile may seem to be straight over the first decade or two, but that one should obtain at least three decades to be certain there is no curvature caused by oxidation holdup. We also plated our samples in an aqueous solution; however, we believe that our preanneal procedure is one of the simplest yet surest experimental methods to prevent oxidation holdup effects. Because of the small size of our samples, we were not able to obtain more than 2 decades of any concentration profile, but the profiles appeared to be straight over this range.

To avoid contributions from surface diffusion it is best to machine at least three diffusion depths from the cylindrical surface of each sample. Unfortunately, it was not possible to take this much material from our small samples. However, some of our early diffusion experiments showed that the lead-oxide coating taken on in the atmosphere was virtually impenetrable to copper for the times and temperatures used in this experiment. Since the cylindrical surface of our samples had such a coating we believe that the effects of surface diffusion were eliminated. A 100-μ-thick cut was taken from the cylindrical surface to insure that no copper on or in this oxide layer was counted.

It may be argued that our method of analysis may be responsible for our small value of ΔH for Cu in Pb; however, similar analysis for Au and Ag in Pb lie well within the uncertainties of other measurements. One additional benefit of making diffusion measurements in lead at high pressure is that the melting temperature of lead increases. Thus, we were able to make diffusion measurements in solid lead over a wider range of temperatures (218–530 °C) than is possible at atmospheric pressure. Moreover, a rather large number of diffusion measurements (75) were made in order to minimize the effects of random errors.

Nachtrieb[26] and co-workers postulated a law of corresponding states as a result of measurements on several diffusion couples to pressures of about 10 kbar. He found that the diffusion constant obeyed an equation of the form

$$D(P, T) = D_0 e^{-bT_m(P)/T} , \qquad (6)$$

where D_0 and b are constants and $T_m(P)$ is the pressure-dependent melting temperature of the alloy. Such a relationship might well be expected for substitutional diffusion if the fraction of vacancies at the melting temperature is independent of pressure. The $\log_{10}$ of the measured diffusion coefficients for Cu, Au, and Ag in lead are plotted as a function of the reduced temperature T_m/T in Fig. 5. The zero-pressure points (open hexagons) and all high-pressure data points of Weyland *et al.*[13] (darkened diamonds) for Au in Pb seem to be randomly distributed about a single straight line independent of pressure. Thus, to within the scatter of the data, the diffusion appears to obey Nachtrieb's relationship. The same can be said for the diffusion of Ag in Pb, where the darkened triangles represent the zero-pressure data and the darkened circles represent all the high-pressure data of Curtin *et al.*[12]

Our data for the diffusion of Cu in Pb have been divided into three pressure ranges. The open diamonds represent the zero-pressure points. The open triangles represent all the data points in the pressure range 19–35 kbar, while the open circles represent all the data in the range 38–56 kbar. Note that there is no overlap between the zero-pressure data and the high-pressure data, and there is no significant overlap between the 19–35-kbar data and the 38–56-kbar data. Clearly Eq. (6) fails to properly describe the pressure dependence of the diffusion of Cu in Pb. This again suggests a fundamental difference between the mechanisms for the diffusion of Au and Ag compared to Cu in Pb, and indicates that a considerable fraction of Au and Ag impurities diffuse by the vacancy mechanism while almost all the Cu impurities diffuse by the interstitial mechanism. This supposition is supported by the work of Rossolimo and Turnbull,[31] who estimate from their quench and resistivity experiments that only about 10–15% of the Au impurity atoms dissolved interstitially in Pb at 300 °C.

The Wert and Zener[36] theory of D_0 for interstitial diffusion relates the entropy of activation ΔS to the preexponential factor D_0. An estimate of ΔS is also obtained by relating the temperature derivative of ΔG to the temperature derivative of the elastic modulus. The corresponding relationships are given by

$$\frac{\Delta S}{R} = \ln \frac{D_0}{(\Delta H a^2/m)^{1/2}} \approx \frac{b \Delta H}{R T_m(0)} , \qquad (7)$$

where a is the lattice constant, m is the mass of the diffusing atom, and b is a dimensionless parameter equal to 0.5 for lead. The value of $\Delta S/R$ as calculated from the middle term in Eq. (7) yields a value of -1.3 ± 0.6, whereas the value calculated from the final expression in Eq. (7) is $+2.3 \pm 0.2$. The discrepancy between the measured and estimated values of ΔS is probably due to the small temperature range (compared to the range obtained for carbon in iron for example) over which diffusion measurements were made.

Figure 6 shows ΔH for Cu in Pb as a function of pressure. From this graph it is seen that the activation energy (enthalpy) increases by about 23% in going from 0 to 60 kbar. Over the same pressure range $\ln D_0$ changes by 3% or less, depending on the temperature. Thus the pressure variation of the diffusion results mainly from changes in the activation energy rather than from changes in the entropy of activation.

Our analysis, which considers all of the data simultaneously, makes it possible to obtain values for the pressure and temperature derivatives of the activation volume. These values are found to be quite uncertain primarily because of the smallness of ΔV along with its relatively large uncertainty. It should be noted, however, that $\partial(\Delta V)/\partial P$ was found to be rather insensitive to the input diffusion parameters, the pressure and temperature corrections, and calibration procedures. On the other hand, $\partial(\Delta V)/\partial T$ was very sensitive to the above variations even to the extent of changing sign. It is thought that the pressure derivative of ΔV as shown in Table I is quite reliable whereas, for the temperature derivative, even the sign is uncertain.

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Symmetry of Quadrupolar Arrangements in Crystals*

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We carry out a new group-theoretical classification of all possible static quadrupolar arrangements in a crystal: We define normal quadrupolar configurations and classify them according to the irreducible representations of the space group of the crystal. This method is a generalization of the representation analysis of magnetic structures, and is equivalent to the method recently proposed by Felsteiner, Litvin, and Zak.

INTRODUCTION

It is well known that the symmetry of electric and magnetic dipolar arrangements may be described from two points of view: the method of Opechowski and Guccione based on the theory of magnetic groups,[1] and the representation theory of crystallographic groups.[2,3] As discussed recently,[4] both of them lead to almost equivalent classifications of all possible dipolar arrangements in a crystal. Moreover, the second one has a thermodynamical aspect, since it is connected with the theory of second-order phase transitions,[5,6] and at the same time has a purely geometrical aspect related to the idea of cryptosymmetry.[7]

Felsteiner, Litvin, and Zak[8] have recently carried out a classification of all possible quadrupolar arrangements in a crystal following the method of Opechowski and Guccione. In this article, it is shown that representation theory may be used as well; normal quadrupolar configurations are defined and classified according to the irreducible representations of the space group of the crystal. According to the discussion given by Opechowski[4] for the case of dipolar arrangements, we may expect the two methods to be equivalent in most cases.

NORMAL QUADRUPOLAR CONFIGURATIONS

Let us consider that each atom i of a crystal on a given sublattice bears a quadrupolar moment characterized by a traceless symmetrical tensor $q^i_{\alpha\beta}$ ($\sum_\alpha q^i_{\alpha\alpha}=0$). These quadrupolar moments may be electrical, as in molecular crystals (in this case each nonpolar molecule is punctualized in $\vec{r}_i$), or may be considered as magnetic as in some rare-earth compounds ($PrAlO_3$, $DyVO_4$, $TbVO_4$,[9]...).

The static interaction energy E_q of the quadrupoles