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Diffusion of Gold in Lead under Hydrostatic Pressure

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Diffusion coefficients of gold in lead single crystals have been determined between 60 and 353°C under hydrostatic pressures ranging from 1 to 10 000 kg cm^{-2}. For each pressure, a unique activation energy for diffusion has been found at all temperatures. Both the pre-exponential factor and the activation energy increase with pressure from values ($D_0=2.5\times10^{-3}$ $\mathrm{cm}^2\,\mathrm{sec}^{-1}$, $Q=8700$ cal/mole) in good agreement with those obtained in previous experiments without pressure, reaching saturation values ($D_0=2.0\times10^{-2}$ $\mathrm{cm}^2\,\mathrm{sec}^{-1}$, $Q=12\,000$ cal/mole) at higher pressures. Correspondingly, the activation volume of the processes involved appears to vary between about 0 and about 24 Å^3/atom in the explored ranges of temperature and pressure. The results seem to indicate that at least two competitive mechanisms are responsible for diffusion in this system and that the relative importance of the two mechanisms depends on the pressure. A simple combination of two mechanisms, which could explain the experimental results, is discussed.

INTRODUCTION

Diffusion coefficients of gold in lead single crystals have been previously measured and the activation energy has been found[1] very low in comparison with that for self-diffusion in lead. An explanation of this result on the basis of the usual "Johnson molecule" vacancy mechanism had been discussed,[2,3] and found to be possible. However, an obvious alternative to the proposed mechanism could be represented by an interstitial mechanism,[4,5] which is not common for diffusion in fcc metals, but could be justified, in the case of the present system, by the relative size of the atoms involved.

Although no experiment has ever been designed to give direct evidence of the atomic mechanism controlling diffusion phenomena, some partial but enlightening information on the subject has been drawn from self-diffusion[6–16] and related[17–22] experiments under hydrostatic pressure. The activation volume of the process can be determined by means of such experiments, and this parameter represents a possibility of discriminating among the mechanisms involved. Some recent calculations[23–29] of the activation volumes associated with the formation and migration of the simplest defects in some fcc metals allow significant comparisons with experimental results.

No pressure experiment had been reported on intermetallic diffusion when we decided to perform the experiment in the gold-lead system which we describe here. During the completion of this work Bonanno and Tomizuka[30] reported similar experiments on the diffusion of In and Sb in Ag, and results on the diffusion of Ag in Pb have now been announced.[31] While discussing

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our results, we shall compare them with those of Refs. 30 and 31.

EXPERIMENT

Pressure Apparatus

Our hydrostatic pressure device is similar to that described by Bridgman.[32] Glycerin was used as pressure-transmitting fluid in the secondary (high-pressure) circuit, throughout the whole temperature and pressure range. The pressure chamber housing the sample is cylindrical, 1.2 cm in diameter and 1.2 cm long, and its wall thickness is 9.4 cm. The manual pump of a hydraulic jack, capable of pressures up to 450 kg cm^{-2}, with mineral oil as transmitting fluid, was used to give pressure to the primary (low-pressure) circuit, and the surface ratio of the pressure-multiplying piston of the hydraulic intensifier is 36.

For each diffusion annealing, pressure was held constant to within $\pm 10\%$ of the nominal, and in most cases within much narrower limits, by manually pumping the primary pump every few hours. The upper limit of the pressure which could be used was set by the difficulty of disassembling the deformed "unsupported area" gaskets.

Pressure was read on an ordinary manometer on the primary circuit, and the nominal value of the secondary pressure was obtained by multiplying this reading by 36. Two checks assured that pressure was effectively exerted on the secondary circuit.

First, the permanent deformation of the low-carbon-steel, "unsupported area" gaskets was found to increase, as expected, with nominal pressure. Second, two soft wax cones (wrapped in aluminum foil to hold their form above their melting temperature) were put inside the cylinder of the hydraulic intensifier, under the larger-diameter part of the mushroom-shaped piston. Should this piston reach its end of stroke (because of compressibility of the secondary fluid or because of a secondary leak, or both), it would deform the cones. Unchanged shape of the cones at the end of each run guaranteed that pressure had been effectively transmitted by the stem of the mushroom to the secondary fluid.

Finally, the fact that the samples were found still single-crystalline and perfectly undeformed at the end of each run assured that the pressure exerted was hydrostatic.

Pressure was applied before switching the heating furnace on and maintained until the chamber was cooled to room temperature.

Heating and Cooling

The high-pressure chamber was heated by an electrical furnace surrounding its external cylindrical surface. The furnace was controlled by an on-off temperature stabilizer whose sensitivity was ±0.4°C. The input signal to this stabilizer was supplied by a thermocouple, at the external cylindrical surface of the pressure chamber wall. The temperature was recorded throughout each annealing run by a second thermocouple, buried in the wall, 7.2 cm from the sample, along the cylindrical axis of the pressure chamber.

A preliminary run at several temperatures in the range of interest, with a third thermocouple on the external surface of the wall 180° from the control thermocouple, and a fourth thermocouple in the sample chamber, assured that: (1) the distribution of the temperature along the cylindrical surface was uniform, i.e., the signal fed to the temperature stabilizer represented well the temperature of the cylindrical surface; (2) the readings of the two axial thermocouples, i.e., the one used to record the temperature during the annealing runs, and the one in the sample chamber, differed by no more than a few °C during the heating and cooling transients and by less than 0.1°C at any steady temperature. The temperature recorded was therefore assumed in every case as the nominal temperature of the sample.

The power supply to the furnace was adjusted for each run to minimize temperature rise time, subject to the requirement of negligible overshoot. Temperature rise times of a few hours were obtained in every case. Cooling times were minimized by lifting the whole pressure apparatus from the furnace and immersing the pressure chamber in a water-cooled oil bath. Cooling times of the order of one hour or less were obtained in every case. Sinusoidal variation of the equilibrium temperature in the sample chamber, due to the on-off furnace control, was always less than the thermocouple sensitivity. The annealing times were therefore corrected only for the heating and cooling times—in a first approximation, by using the diffusion parameters D_0 and Q previously measured *in vacuo*,[1] and in a second approximation by using the parameters obtained from the first approximation.

Sample Preparation and Analysis of the Penetration Curves

A radioactive-tracer method and sectioning technique were adopted. The following technical details were assembled from those used in previous works.[1,33]

About 1000 atomic layers of ordinary, nonradioactive gold were electroplated on one of the flat surfaces of 99.999% pure lead single crystals.[34] The single crystals were cylindrical, 1.1 cm in diameter and 1.1 cm long. Annealing times were so chosen, for the higher temperatures, that the time correction for temperature

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[32] P. W. Bridgman, *The Physics of High Pressure* (G. Bell & Sons, London, 1958), p. 42.

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transients would be small compared with the total annealing time, and maximum penetration distances (as defined in Ref. 1) of about 5 mm resulted. For lower temperatures, times were chosen so as to obtain minimum penetration distances (see Ref. 1) of about 2 mm. After annealing, 92 slices were microtome-cut from each sample and laid in a specially designed polyethylene slice-holder that held them within a uniform-flux region (1 cm long×3 cm diam) of an L54 reactor. Thickness of the slices was 50 μ for most samples, except for those diffused at lower temperatures, for which it was reduced to 40 μ and in one case to 20 μ. After reactor activation, the 411.8-keV γ activity of $^{198}Au^+$ in the slices was measured with a scintillation counter and a single-channel analyzer. The activity of each slice was measured separately, so that a 92-point penetration Gaussian was obtained for each sample. From the activity of the last slices of each sample it could be verified that the contribution of other activities (lead and impurities) to the above-mentioned energy peak was negligible. Total counting time for each sample was short enough (130 min) for the decay correction of $^{198}Au^+$ (2.7-day half-life) to be negligible.

For all other experimental details the reader may consult Refs. 1, 33, and 34.

RESULTS

Figure 1 summarizes the results. The straight line in each plot represents the least-squares adjustment of all experimental points at the given pressure. It can be seen that, for each pressure, the activation energy is the same, within experimental errors, at all temperatures. The scatter of the points, satisfactorily low at the first five pressures, is higher at 10 000 kg cm^{-2}, showing the limit of usability of the apparatus. Only four diffusion runs were performed at atmospheric pressure, because it was checked that their results fit, within errors, the parameters already determined *in vacuo*.[1,33] This assures that little or no effect on diffusion must be attributed to the presence of the glycerin around the sample, or to other features of the apparatus and procedure.

The pre-exponential factors D_0 and the activation energies Q, obtained from the Arrhenius straight lines of Fig. 1, are plotted versus pressure in Fig. 2. It can be seen that they both increase with pressure from $D_0=2.5\times10^{-3}$ cm^2 sec^{-1}, $Q=(8730\pm200)$ cal/mole at 1 kg cm^{-2} to $D_0=2\times10^{-2}$ cm^2 sec^{-1}, $Q=(11\,990\pm100)$ cal/mole at 8000 kg cm^{-2}, at which pressure they reach a saturation. It can also be noted that the values of both parameters vary slowly up to 4000 kg cm^{-2}, showing a step-like increase around 6000 kg cm^{-2}.

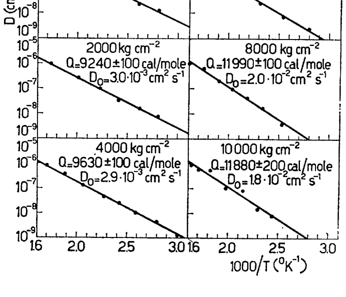

FIG. 1. Dependence of the measured diffusion coefficient D on temperature and pressure.

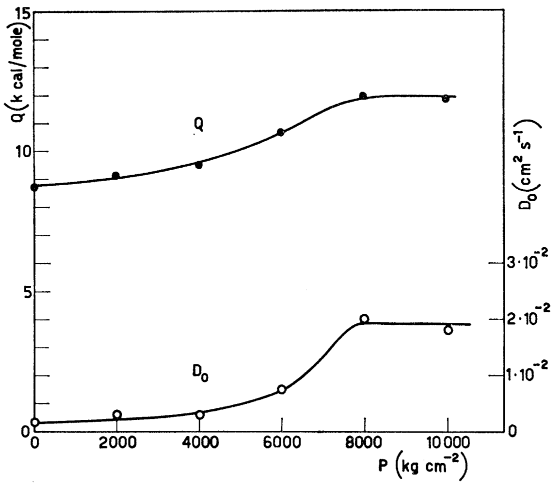

FIG. 2. Dependence of the activation energy Q and pre-exponential factor D_0, as obtained from the experimental graphs of Fig. 1, on the annealing pressure.

Intersection of the Arrhenius plots of Fig. 1 at arbitrary constant values of temperature gives the curves ln$D$ versus P represented in Fig. 3. The value of the activation volume[6] ΔV_a of the process involved at any temperature and pressure can be obtained from the slope of these curves. It can be noticed that ΔV_a is positive at low pressure and practically zero at high pressure. The transition between the two slopes is smooth and not well defined at the higher temperatures, whereas at the lower temperatures it becomes sharp, giving rise to a maximum of ΔV_a around 7000 kg cm^{-2}. This maximum increases with decreasing temperature, reaching approximately 24 Å^3/atom around 100°C. Conversely, the value of ΔV_a at low pressure decreases very little with decreasing temperature, passing from about 14 Å^3/atom around 300°C to about 10 Å^3/atom around 100°C.

DISCUSSION

General Considerations

The theoretical background of pressure experiments on point defects has been treated[22–29,35,36] and the formulas of interest have been extensively recalled in

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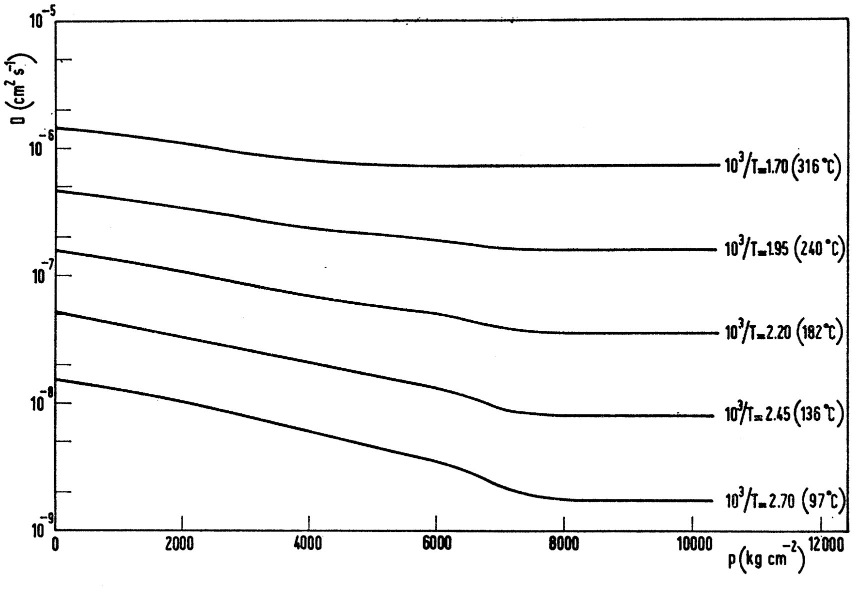

FIG. 3. Dependence of D on pressure at five given temperatures. The D values plotted here were obtained from the best-fit straight lines of Fig. 1. The slopes of the curves presented are proportional to the apparent activation volumes of the processes in each temperature and pressure condition.

several experimental articles.[6–9,11,13,15,19,21,22] The logarithmic derivatives of the lattice parameter and vibrational frequency with pressure have been estimated for lead,[11] gold,[19] and some fcc alloys,[13,21] and found to be small, or of the order of very few percent of the logarithmic derivative of the total measured quantities (diffusion coefficient, annealing rate, or relaxation time). Consequently, the logarithmic derivatives of these total quantities are currently assumed as a measure of the activation volume of the process. If the measured quantity is the diffusion coefficient D, one can write

$$\Delta V=(\partial\Delta G/\partial P)_T\simeq RT(\partial \ln D/\partial P)_T,$$

where ΔG is the free energy of activation, P the pressure, T the temperature, and R the gas constant.

Extensive calculations have been carried out for the energies and the lattice distortions associated with the various stable and saddle-point configurations in copper,[37] and vacancy relaxation has also been dealt with in other fcc and bcc metals.[38] Calculations on impurity-vacancy binding and interchange and on impurity interstitial trapping and mobility[39] provide a platform for interpretation of impurity-diffusion experiments.

The interpretation of self-diffusion and intermetallic diffusion in pure metals and in substitutional alloys is usually based on vacancy mechanisms—obviously because such high energy (in comparison with vacancies) is required to form thermal-equilibrium interstitials that they are numerically negligible wherever they must be thermally activated. Small impurity atoms, or atoms of elements crystallizing in systems different from that of the solvent, usually take interstitial positions at any temperature, with no possibility of passing to substitutional positions, and they migrate interstitially. Analogously, large impurity atoms, especially if capable of crystallizing in the same system as the solvent, usually take only substitutional positions at any temperature, and they need a vacancy to acquire mobility. It seems to us, however, that attention should be paid to the possibility that, for intermediate differences is size between isomorphic solvent and solute (lead and gold, for instance), the lattice stresses caused by the presence of a solute atom in a substitutional or in an interstitial position are comparable, and the energy required for a substitutional solute atom to pass to an interstitial position is so low that the two configurations can coexist. The high mobility of interstitial atoms (the calculated energy of motion of interstitials in fcc metals is of the order of 0.05–0.1 eV against ≈0.4–1.3 eV for vacancies[37,39]) might then enhance the efficiency of interstitial matter transport, even in competition with more numerous vacancies.

The equilibrium between coexisting configurations, and the relative efficiency of migration mechanisms, might be temperature-dependent, and in fact the two mechanisms have been postulated to act in different temperature intervals[40] to explain anomalous experimental findings on copper diffusing in germanium.[40,41]

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[37] See Ref. 27 and the numerous articles cited there.

[38] L. A. Girifalco and J. R. Streetman, J. Phys. Chem. Solids **4**, 182 (1958); L. A. Girifalco and V. G. Weizer, *ibid.* **12**, 260 (1960).

[39] For a comprehensive summary see A. C. Damask and G. J. Dienes, *Point Defects in Metals* (Gordon & Breach, Science Publishers, Inc., New York, 1963).

[40] F. Van der Maesen and J. A. Brenkman, J. Electrochem. Soc. **102**, 229 (1955); B. I. Boltaks, Zh. Tekhn. Fiz. **26**, 457 (1956) [English transl.: Soviet Phys.—Tech. Phys. **1**, 443 (1957)]; F. C. Frank and D. Turnbull, Phys. Rev. **104**, 617 (1956); K. Weiser, *ibid.* **126**, 1427 (1962).

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Similar, temperature-dependent equilibrium and relative efficiency, if found in metals, should be ascribed to differences in the potential energies (associated with lattice distortions and possibly with electronic rearrangements around stable defects and/or around saddle points) due to impurity-vacancy complexes and the said potential energies due to interstitial impurities. Conversely, if the difference between the above potential energies is little, the two mechanisms can be simultaneously active throughout the whole measured temperature interval, and if this interval is rather narrow, as it is necessarily when the parent metal has a low melting point, it might even be impossible to distinguish them in the isobar Arrhenius plots.

Owing to large possible differences between the pairwise interactions exerted among solvent atoms and those exerted between solvent and solute atoms, a small difference in potential energy does not necessarily imply a small difference in lattice distortion. In fact, the relative contribution of solvent-solvent and solvent-solute interactions to the relationship between lattice distortion and the associated energy increment can be remarkably different for the two configurations. Processes indistinguishable by their activation energies might then be distinguishable by their activation volumes.

On the basis of the above considerations, all the experimental results presented in the previous section can be explained. It is unfortunate that no complete set of calculated formation and migration volumes for vacancies and interstitials in doped metals is available for direct comparison with these results. The only calculation available is that for pure copper.[22–28] However, comparison of these calculated results with the values measured as a function of pressure in the present work looks interesting. Taking the values of Johnson and Brown[27] as representative of an average of the theoretical results for copper, the total formation volumes for a vacancy and for an interstitial (including the appearance or disappearance of an atom at the surface of the crystal) are both positive, respectively, of the order of $+0.52V$ (V=atomic volume) and of $+1.2V$; the migration volume of a vacancy is also positive, of the order of $+0.25V$, while only the migration volume of an interstitial is practically zero or very slightly negative. Activation volumes in pure copper should therefore be expected to be $+0.77V$ for self-diffusion, and about zero for migration of pre-existing interstitials (such as, for instance, frozen-in, irradiation-produced copper interstitials).

If we try to extrapolate these results to an impure metal, imagining, as has been postulated[2] in the case of interest here, a weaker repulsive interaction between solute and solvent atoms than between solvent and solvent atoms, we should expect an activation volume for diffusion of the solute by a vacancy mechanism slightly lower than that for self-diffusion, because the formation volume should be nearly unchanged, and the migration volume should be smaller for the impurity-vacancy complex than for the vacancy alone. The migration volume of interstitial impurities would probably remain nearly zero or very slightly negative. Most pressure-diffusion experiments of interstitial impurities in bcc metals[14,15] gave activation volumes equal to zero or to a small fraction of the atomic volume of the dissolved atom.

Interpretation of the Results

To interpret the results of the present experiment, we suppose that gold impurities can take both substitutional and interstitial positions in lead, with comparable energies of dissolution. Substitutional atoms migrate by a "deviated-path" vacancy mechanism,[2,3] whereas interstitial atoms require only the migration energy to diffuse, so that they both can diffuse with the low activation energies that have been measured *in vacuo*[1,33] and at low pressures (present work). At low pressures the activation volume (Fig. 3), between $+0.33V$ and $+0.47V$, might well indicate a vacancy-diffusion mechanism, with a small contribution of interstitial diffusion. (For comparison, the calculated formation volume of a vacancy in pure lead is $0.55V$[23]; the measured self-diffusion volume in pure lead is $0.64V$[11] to $0.71V$.[8]) With increasing pressure, diffusion coefficients decrease and the activation energy increases, as expected. The contribution from interstitial diffusion is needed to explain the zero activation volume at high pressures. In fact, as pressure increases, it can be expected that the "deviated-path" model[3] loses its efficiency, because the four atoms (three solvent and one solute atom), through which the jumping atom must pass in the solvent-vacancy interchange (see Fig. 1 of Ref. 3), approach one another sufficiently that even when deviating towards the impurity atom, the jumping solvent atom must come closer to them than the nearest neighbor. There must be, therefore, some threshold value of pressure, above which the energy for impurity diffusion by vacancies increases more than linearly with pressure, stepping up to the values that would be expected without the "deviated-path" model. According to our interpretation, above this pressure, only interstitials are practically effective. The value of the diffusion coefficient is lowered to the contribution of interstitials only, with an apparent step-like increase in diffusion energy (Fig. 2) to the value characteristic of interstitial mechanism at that pressure, and the activation volume is zero, as expected for interstitial migration.

The high value of the slope of the curves of Fig. 3 at intermediate pressures and low temperatures has no physical meaning as a real activation volume, because it is not a feature of a single mechanism, but it actually represents the transition between two mechanisms.

The fact that diffusion energy appears higher under the conditions in which we postulate an interstitial mechanism than under the conditions in which we postulate a vacancy mechanism is not in disagreement with the universally accepted fact that the migration energy for interstitials is much lower than for vacancies.[37,39] In fact, this latter conclusion is based on theoretical and experimental results, all comparing the mobility of interstitials with that of ordinary "non-deviated-path" vacancies, and we explicitly admit that, when the "deviated-path" model loses its efficacy, the vacancy migration energy steps higher than the migration energy of interstitials, so that the interstitial mechanism starts to control diffusion.

We discussed before why the contribution of interstitial diffusion is needed to explain all our results. Let us add now that an interstitial mechanism alone would not be sufficient, because it would not explain the positive value of the activation volume at low pressure, followed by a zero activation volume at high pressure. In fact, the migration volume for interstitial impurities can be expected to be zero or slightly negative by analogy with the value calculated for the migration of interstitials in pure copper, or it could even be expected to be positive, as measured, owing to the unknown interaction between solvent and solute. But we can imagine no simple reason explaining the measured abrupt change in the trend of activation volume with pressure, if this volume had to be attributed to the migration of interstitials only.

The pressure dependence of the frequency factor D_0, shown in Fig. 2, is consistent with the two-model interpretation proposed here. This pre-exponential factor should actually depend very little on pressure for a given mechanism, but may well have a different value for each mechanism.

Comparison with the Results of Other Intermetallic-Diffusion Experiments under Hydrostatic Pressure

Two sets of data have recently been reported[30] or announced[31] on this subject. Our results are substantially in agreement with both sets, although they are more directly comparable with the results of Curtin *et al.* than with those of Bonanno and Tomizuka. All three sets of results, including ours, show that, with increasing pressure, the diffusion rates decrease and the activation energy increases. However, there is no indication of a two-mechanism model in the conclusions of Bonanno and Tomizuka, whereas the same two-mechanism model, based on a combination of interstitials and vacancies at low pressure and interstitials only at high pressure, is taken into account both by Curtin *et al.* and by us. The reasons for this difference seem quite clear to us: first of all, Bonanno and Tomizuka study the diffusion of different tracers into Ag and find that the results can be explained by the Lazarus theory of impurity diffusion as modified by Le Claire.[29] This theory directs attention to the electrostatic interaction between an impurity and a vacancy. However, it is recognized in Le Claire's work that the calculations based on this theory agree satisfactorily with experimental results only if the parent metal is a noble metal, as is the case of Bonanno and Tomizuka's experiment. It is therefore natural to expect a closer correspondence between our results and those of Curtin *et al.*, who use the same (non-noble) parent metal, than between Bonanno and Tomizuka's results and ours. It might prove interesting to extend the Lazarus–Le Claire concepts (on the effects of the above-mentioned electrostatic interaction on diffusion properties) to systems in which the parent metal has a more complicated electronic structure than noble metals. However, too few details are known about the electronic structure of lead to attempt a solution of the problem in the case of this metal, and, as far as we know, diffusion mechanisms in this solvent have been dealt with only on the basis of lattice distortions. Having read only an abstract of their work, we do not know whether Curtin *et al.* discuss the relationship of their results to Bonanno and Tomizuka's; neither do we know whether they make an effort to apply the Lazarus–Le Claire theory to their own findings. At present, we feel that it would be beyond the scope of the present work to try to make such an effort with our experimental results.

There is a second reason for our results' being more closely comparable with those of Curtin *et al.* than with those of Bonanno and Tomizuka. The latter reported pressure-diffusion experiments only at 910°C, a temperature rather close to the melting point of the parent metal. It can be seen in Fig. 3 of the present work that at a high temperature the separation of the two mechanisms is less sharply shown by the experiment than at a low temperature. The uniqueness of the mechanism pointed out by Bonanno and Tomizuka might therefore become less apparent on the basis of low-temperature measurements. In this respect it may be significant that step-like curves similar to those of Fig. 3 of the present work might be drawn through the experimental points displayed by Fig. 2 of Ref. 30 for impurity diffusion, the step being located around 6 kbars as it is in our results, and this is possibly outside the experimental errors since the same is not possible for the self-diffusion points on the same Fig. 2 of Ref. 30, through which only a clear straight line can be drawn.

A further observation is suggested by the present comparison: The pressure of our experiment and of Bonanno and Tomizuka's is confined to about 10 kbar or below, whereas Curtin *et al.* reached about 40 kbar, but they found no change in the volume of activation above 11.9 kbar. It may be concluded that, at least insofar as lead is used as the parent metal, the suggested suppression of the vacancy contribution should be located in the neighborhood of 10 kbar, and the repetition of our experiment at higher pressures (up to 40 kbar) is not likely to supply much further information.

CONCLUSIONS

In summation, we suppose that gold impurity can take both substitutional and interstitial positions in lead. Substitutional gold migrates by a "deviated-path" vacancy model, and interstitials migrate interstitially. At low pressures both mechanisms operate simultaneously with inseparable activation energies, the former mechanism being more effective than the latter. At high pressures only interstitials keep migrating, while the contribution from the vacancy mechanism becomes negligible.

In our experiment the temperature interval of the diffusion measurements has been extended to very low values: The experimental point at 60°C in the 4000 kg cm^{-2} plot (Fig. 1), perfectly fitting the same Arrhenius straight line as all other points at the same pressure, rules out the contribution, once postulated,[5] of diffusion along internal surfaces, at least in the gold-lead system.

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Calculation of Thermal Conductivity by the Kubo Formula

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The Kubo expression for lattice thermal conductivity is analyzed by the method of the double-time Green's function. The usual relaxation-time formula of kinetic theory can be obtained from the Kubo formula by suitable approximations only.

1. INTRODUCTION

The Kubo formula for the thermal conductivity is

$$K=\frac{k\beta}{3\Omega}\int_0^\infty dt\int_0^\beta d\lambda\langle\mathbf{Q}\cdot\mathbf{Q}(t+i\lambda)\rangle\,,\qquad(1)$$

where $\mathbf{Q}(t)$ is the energy-flow vector operator at time t and the brackets $\langle\ \rangle$ stand for thermodynamic averaging, namely, for any operator O

$$\langle O\rangle=\mathrm{Tr}e^{-\beta H}O/\mathrm{Tr}e^{-\beta H}\,,$$

where H is the Hamiltonian of the system, and $\beta=(kT)^{-1}$.

Recently Luttinger[1] has given a "mechanical" derivation of this expression by introducing a varying gravitational field. In principle, Eq. (1) is more general than any transport equation. For a lattice, the energy-flow vector has also been rigorously deduced by Choquard[2] and for the spherically symmetric dispersion formula, it is the usual Peierls expression

$$\mathbf{Q}(t)=\sum_{\mathbf{k},j}\mathbf{v}_{\mathbf{k},j}\omega_{\mathbf{k},j}n_{\mathbf{k},j(t)}\,,\qquad(2)$$

in units with $\hbar=1$; $\mathbf{v}_{\mathbf{k},j}=\nabla_{\mathbf{k}}\omega_{\mathbf{k}j}$ is the group velocity, $\omega_{\mathbf{k}j}$ is the energy of the kth normal mode in the jth branch, and $n_{\mathbf{k},j}=a_{\mathbf{k}j}{}^\dagger a_{\mathbf{k}j}$ is the number-density operator of the phonons in the second-quantized form. Thus, by the works of Luttinger and Choquard, it is possible to compute lattice thermal conductivity from the general expression

$$K=\frac{k\beta}{3\Omega}\sum_{\mathbf{k},j}\sum_{\mathbf{q},j'}\int_0^\infty dt\int_0^\beta d\lambda\,\mathbf{v}_{\mathbf{k},j}\cdot\mathbf{v}_{\mathbf{q},j'}\times\omega_{\mathbf{k},j}\omega_{\mathbf{q},j'}F_{\mathbf{k},j;\mathbf{q},j'}(t+i\lambda)\,,\qquad(3)$$

where

$$F_{\mathbf{k},j;\mathbf{q}j'}(t+i\lambda)=\langle n_{\mathbf{k}j}(0)n_{\mathbf{q}j'}(t+i\lambda)\rangle\,.\qquad(4)$$

Essentially one has to calculate the correlation function of two number-density operators at different times. In this paper we shall discuss an approximation scheme which leads to the relaxation-time formula of kinetic theory for thermal conductivity as it has been reviewed and discussed by Carruthers.[3]

2. RETARDED TWO-PARTICLE GREEN'S FUNCTION

The correlation function $F_{\mathbf{k},j;\mathbf{q}j'}(t)$ is an integral over the Fourier transform of the associated Green's function

$$G_{kk,q}(t-t')=-i\theta(t-t')\langle[n_k(t),n_q(t')]\rangle\equiv\langle\langle n_k(t),n_q(t')\rangle\rangle\,.$$

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