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Isotope Effect for the Diffusion of Cadmium in Lead

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This experiment to determine the isotope effect for diffusion of Cd^{109} and Cd^{115m} in pure lead was performed as a critical test of the proposed interstitial-vacancy pair mechanism of solute diffusion. The relative diffusivity of the two radioisotopes was determined, after sectioning, by counting with a thin NaI detector system, using energy discrimination. Stability and reproducibility of the count rates were tested and verified, an upper limit on the effect of crossover shown to be negligible, and a zero-isotope-effect experiment performed successfully. The isotope effect for the volume diffusion of cadmium in lead was determined to be $(D_{109}/D_{115m}-1)=0.0032\pm0.001$ at 248°C, corresponding to a solute correlation factor $f=0.12$ for a mechanism involving single atomic jumps. It is then shown that this result, together with previous results for the solute and self-diffusivities D_2^0 and D_1^0 and the linear-enhancement factor b_{11} for self-diffusion, are inconsistent with the simple vacancy, interstitial, interchange, and ring mechanisms of solute diffusion, but agree with predictions of the model for solute diffusion by means of interstitial solute-vacancy pairs. The migration of associated vacancies results in a strong correlation of successive atomic jumps of bound interstitial solute atoms.

I. INTRODUCTION

The isotope effect (D_a/D_b-1) for diffusion of two chemically equivalent isotopes a and b in a crystalline solid is determined by the correlation factor f_a of the diffusion according to

$$D_a/D_b-1=f_a(w_a/w_b-1), \tag{1}$$

provided that the jump direction is an axis of twofold symmetry in the crystal and that the fractional changes of jump frequency and correlation factor between the two isotopes are small.[1,2] D_a and D_b are the isotopic diffusion constants, and w_a and w_b are the isotopic jump frequencies. Since atomic jump frequencies are a statistical fluctuation of particular normal vibrational modes of the lattice, such jump frequencies are, like the vibrational frequencies, inversely proportional to the square root of the mass of the atom or atoms participating in a jump. For a general diffusion mechanism involving the simultaneous motion of n atoms,[3,4]

$$\frac{w_a}{w_b}-1=\Delta K\left[\left(\frac{(n-1)m_0+m_b}{(n-1)m_0+m_a}\right)^{1/2}-1\right]. \tag{2}$$

Here m_a and m_b are the respective isotopic masses, m_0 is the average mass of the host atoms, and ΔK is the fraction of translational kinetic energy in the unstable mode which results in an atomic jump.[5]

The isotope effect for metallic diffusion is sufficiently small that it cannot be accurately measured by separate determinations of D_a and D_b. The error arising from separate measurements of time, temperature, and the distance may be avoided, however, by diffusing both isotopes simultaneously in the same specimen. If the boundary conditions for diffusion of the two isotopes are such that the resultant penetration is Gaussian, i.e., that the concentration of each isotope varies with the distance x from an initially planar-surface source according to

$$C_a=C_a^0e^{-(x^2/4D_at)}, \tag{3}$$

it may easily be shown that

$$\ln(C_a/C_b)=-(D_a/D_b-1)\ln(C_a)+\text{const}. \tag{4}$$

Such a Gaussian dependence of tracer concentration is assured if the diffusion source dissolves entirely in the host lattice in a time which is very short compared to the total diffusion time.[6] After the simultaneous diffusion of both isotopes, the specimen may be sectioned and the concentrations C_a and C_b determined accurately for each section by means of the isotopic activities. If the two isotopes are of sufficiently different atomic masses, and proper techniques can be developed to accurately measure the activity of each isotope in the presence of the other, the quantity (D_a/D_b-1) may then be determined from the slope of the plot of $\ln(C_a/C_b)$ versus $\ln(C_a)$.

The two cadmium isotopes Cd^{109} and Cd^{115m} were selected for this experiment primarily because the difference in their atomic masses is large enough to allow an observable effect. In addition, the half-lives of both are long enough that there is no serious time limitation on the experiment.

Once the isotope effect has been measured experimentally, the product $f_a\Delta K$ may be calculated from

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[1] A. H. Schoen, Phys. Rev. Letters **1**, 138 (1958).

[2] K. Tharmalingam and A. B. Lidiard, Phil. Mag. **4**, 899 (1959).

[3] J. G. Mullen, Phys. Rev. **121**, 1649 (1961).

[4] G. H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957).

[5] A. D. LeClaire, Phil. Mag. **14**, 1271 (1966).

[6] G. V. Kidson, Phil. Mag. **13**, 247 (1966).

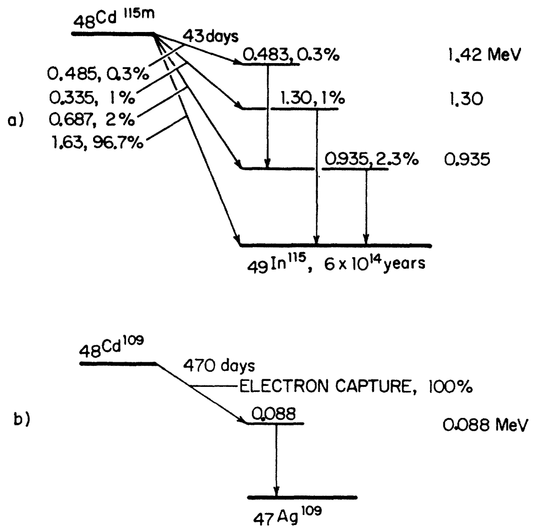

FIG. 1. Relevant portions of the decay schemes for (a) Cd^{115m} and (b) Cd^{109}.

Eqs. (1) and (2) for any assumed diffusion mechanism. There are no suitable isotopes for a measurement of ΔK for lead self-diffusion, and hence no reliable means of estimating ΔK for impurity diffusion in lead.[7] Nevertheless, measurements of ΔK for self-diffusion in other fcc metals[8–10] are very close to unity. We shall assume that $\Delta K=1$. Since both f_a and ΔK are positive-definite quantities which may not exceed unity, an assumed mechanism must be incorrect if the resultant value of f_a is greater than unity. An experimental result might also lead to an unreasonably small value of f_a for a particular mechanism. In this case, it is unlikely that the observed diffusion occurs by this mechanism.

The fast diffusion of cadmium in lead and the relatively small linear enhancement of lead self-diffusion by cadmium additions are inconsistent with the simple vacancy mechanism of impurity diffusion.[11] To explain the experimental results, it was proposed that cadmium dissolves in lead dissociatively[12] in the same manner as the noble-metal solutes,[13,14] but that the divalent cadmium ions are strongly attracted to vacancies by a screened electrostatic interaction. A detailed thermodynamic and kinetic model has been presented for the diffusion of solute and solvent in the presence of such interstitial solute-vacancy pair defects.[15] The resultant linear-enhancement factor for self-diffusion

$$b_{11}=f_0D_2^0/D_1^0 \tag{5}$$

agrees closely with the experimental observations, thus strongly supporting the proposal. The migration of solute by this mechanism is very correlated due to associated vacancy-solvent exchange jumps, so that the solute correlation factor as determined by the isotope effect must be very small.

II. SPECTROSCOPIC CONSIDERATIONS

The relevant portion of the Cd^{115m} decay scheme is shown in Fig. 1(a),[16] and that for Cd^{109} in Fig. 1(b).[17] The 88-keV γ ray of Cd^{109} is highly converted ($>95\%$ [17]), which gives rise to a 22-keV K x ray of Ag^{109}. The 88-keV γ ray of Cd^{109} was used to measure the activity of the slices relative to each other. To measure the relative activities of the two isotopes in each slice, we used the 22-keV x ray of Ag^{109} and the 1.63-MeV β ray of Cd^{115m}.

In order to count the γ ray and the x ray independently of the β rays, a Plexiglas filter was used to stop the β rays. The range of 1.63-MeV β rays[18] is 0.751 g/cm^2. The density of the Plexiglas was determined to be 1.17 g/cm^3, so that the range of the β rays in the Plexiglas is 6.5 mm. Thicknesses of 7.0 and 7.5 mm, corresponding to 0.819 and 0.878 g/cm^2, were used to stop the β rays for counting of the γ and x ray, respectively. An upper limit for the attenuation of the γ and x ray by these filters may be calculated by assuming that the Plexiglas is 100% oxygen; the resultant attenuations are 13.7 and 51%, respectively.[19] Attenuation of the 22-keV x ray was determined experimentally to be about 30%.

III. EXPERIMENTAL PROCEDURE

A. Diffusion Experiment

The maximum isotope effect for the diffusion of Cd^{109} and Cd^{115m} in lead is given by

$$D_a/D_b-1=(m_a/m_b)^{1/2}-1=0.027154. \tag{6}$$

This maximum effect should be observed if cadmium diffuses by the interstitial mechanism, for which $f_a=1$ and $n=1$. For such a small effect to be experimentally measurable, the ratio C_a/C_b must be determined within a very small experimental error, and over a range in the concentration C_a of several orders of magnitude.

Experiments to determine the diffusivity of cadmium in lead[11] revealed that the Gaussian penetration is

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[8] N. L. Peterson and L. W. Barr (unpublished).

[9] N. L. Peterson, Phys. Rev. **136**, A568 (1964).

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[12] F. C. Frank and D. Turnbull, Phys. Rev. **104**, 617 (1956).

[13] B. F. Dyson, T. Anthony, and D. Turnbull, J. Appl. Phys. **37**, 2370 (1966).

[14] T. R. Anthony and D. Turnbull, Appl. Phys. Letters **8**, 120 (1966).

[15] J. W. Miller, preceding paper, Phys. Rev. **188**, 1074 (1969).

[16] *Nuclear Data Sheets*, compiled by K. Way *et al.* (National Academy of Sciences–National Research Council, Washington D. C., 1958), NRC 60-3-104; 60-3-108; 60-3-109; 60-3-110.

[17] *Nuclear Data Sheets*, complied by K. Way *et al.* (National Academy of Sciences–National Research Council, Washington, D. C., 1958), NCR 60-2-47; 60-2-48; 60-2-54; 60-2-55; 60-2-56.

[18] E. Fermi, *Nuclear Physics* (University of Chicago Press, Chicago, 1950), p. 32.

[19] C. M. Davisson, *K. Siegbahn, Alpha-, Beta-, and Gamma-Ray Spectroscopy* (North-Holland Publishing Co., Amsterdam, 1965), p. 827.

representative of the true volume-diffusion constant. The effect of dislocation diffusion, when observed, is a non-Gaussian "tail" at greater depths where the isotopic concentrations are sufficiently small that a majority of the tracer atoms may have spent a significant fraction of the total diffusion time diffusing by a dislocation mechanism. Both the range of the Gaussian penetration and the depth at which dislocation tails might be observed may thus be increased greatly by depositing larger quantities of cadmium isotope. This has been verified experimentally. It is, therefore, necessary to deposit a large total activity of both isotopes on the specimen surface in order to assure a Gaussian penetration, representative of the volume-diffusion mechanism, over the greatest possible range of the concentration C_a. This requirement is consistent with the desirability of large final specific activities for the accurate determination of C_a/C_b. Measurements of the ratio C_a/C_b must accordingly be confined to the region of Gaussian penetration for both isotopes.

A single crystal of lead was grown from the melt using 99.9999% pure lead. This crystal, of 1-cm^2 cross section, was then annealed at 280°C for two days. A specimen for diffusion was cut from this crystal by a spark-cutting technique. Just prior to electrodeposition of the cadmium isotopes, one surface of the sample was microtomed flat within about 0.5 μ, and polished gently with a small dry swab of soft cotton to remove any surface oxide film.

Nearly equal total activities of the Cd^{109} and Cd^{115m} isotopes were dissolved in a cyanide electroplating solution, in which NH_4OH was used to obtain the desired pH of 10.5.[20] After electrodeposition of both isotopes on the microtomed surface, the resultant activity of this surface was determined to be greater than 10^7 counts per minute for each isotope. The specimen was then sealed in an evacuated Pyrex tube and annealed at a constant temperature of 248°C for 50 min. After quenching, all surfaces except the one initially electroplated were etched with a solution of acetic acid and hydrogen peroxide to remove all traces of any possible surface diffusion. The active face of the specimen was then leveled with respect to the plane of motion of the microtome blade for final sectioning. Sections of 3-μ thickness were cut from the sample and accurately weighed. The specimen cross-sectional area was determined from micrometer measurements of the diameter.

B. Apparatus

A block diagram of the apparatus is shown in Fig. 2. The scintillation detector is a $3\times3\times\frac{1}{4}$ in.[3] NaI(Tl) crystal integrally mounted on a Dumont 6363 phototube by the Harshaw Chemical Co. The detector has a thin Al window of 1-mil thickness. An additional 1-mil thickness of Al foil was placed over the detector when it was discovered that the original detector window had a light leak.

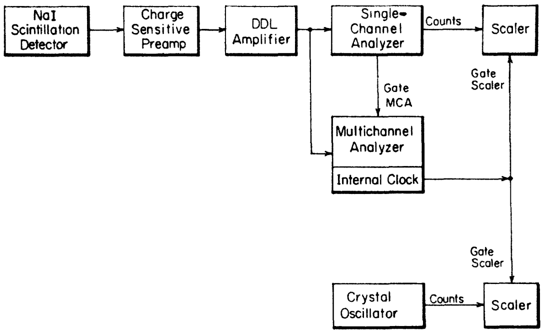

FIG. 2. Block diagram of the counting apparatus.

The single-channel analyzer has a fixed dead time of 3 μsec. The multichannel analyzer was gated by the single-channel analyzer so that the portion of the spectrum being counted could also be seen on the multichannel-analyzer *CRT* display. The crystal oscillator was used in conjunction with one scaler to measure the elapsed time precisely. The sample holder is a Plexiglas box in which the detector is rigidly mounted.

C. Measurement of the Cd^{109} Specific Activity

The variation of the absolute isotopic concentration $C_a = C_{109}$ from slice to slice may be inferred from a measurement of the corresponding variation of specific activity. This may be accomplished by precise measurement of the total Cd^{109} activity of each slice in its entirety, and dividing by the sample weight.

Preliminary measurements of the activity of the 22-keV x ray and the Cd^{115m} β radiation of each slice showed that it would be necessary to combine adjacent slices, especially those of smaller activity, in order that there be enough total activity in each sample for subsequent measurement of the ratio C_a/C_b. It was also determined that the deviations in thickness, from slice to slice, are sufficiently great for such thin slices that counting techniques could not be used effectively for these slices in metallic form. Both the 22-keV x ray and the Cd^{115m} β radiation are attenuated sufficiently by μ thicknesses of lead that counting of the samples in this form gives results dependent on the slice thickness.

For this reason, each sample was completely dissolved in 0.5 ml of an acetic acid and hydrogen peroxide solution, in a thin-walled 3-ml centrifuge tube. The 88-keV γ radiation of Cd^{109} was used to measure C_{109}, since this radiation is less sensitive to the unequal concentrations of lead ions in the solutions than is the 22-keV x ray. A sample holder was designed to serve as both a β filter and a fixed geometry for the centrifuge tubes. A cylindrical Plexiglas rod was drilled out along its center to permit insertion of the centrifuge tubes,

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[20] J. W. Miller, Ph.D. thesis, Harvard University, 1969 (unpublished).

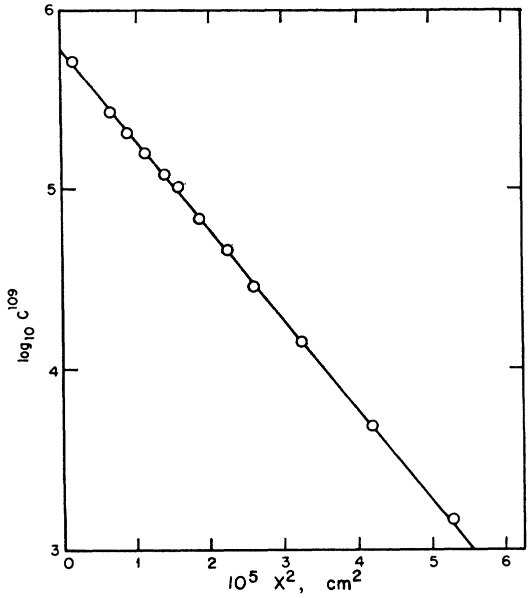

FIG. 3. Gaussian penetration profile of Cd^{109} diffusion in pure lead at 248°C, for determination of the isotope effect.

and mounted in a fixed position with respect to the detector. The final wall thickness of the Plexiglas sample holder was 7 mm, sufficient to stop the β radiation. Energy discrimination was used to isolate and count the activity of this 88-keV radiation, with the window set from approximately 62–170 keV. Before proceeding to count each sample, the stability of the counting rate and the reproducibility of data were tested; since the standard deviation of the resultant data was very nearly that of counting statistics, both tests were satisfactory.

In order to maintain a check on both stability and reproducibility during the counting, the first sample was recounted at intervals during the run, and each sample counted twice. The resultant activities were then corrected for dead time and background, and divided by the slice weights to determine the specific activities C_{109}. Values of $\log_{10}(C_{109})$ for each sample are plotted versus the corresponding values of x^2, the square of the penetration distance in Fig. 3. The Gaussian behavior of the diffusion is thus verified by the linearity of the plot, and calculated values of $\ln C_{109}$ are to be used in the determination of the isotope effect according to Eq. (4).

It is also necessary to verify the Gaussian behavior of the diffusion of isotope b, Cd^{115m}. To permit counting of the β radiation of Cd^{115m}, a new sample holder was designed such that the detector was not shielded from the centrifuge tubes, and energy discrimination used so that only the β radiation would be counted. The window was set from about 225 keV to about 1.4 MeV. As for the measurement of C_{109}, stability and reproducibility were tested, and checked during the counting. The results were corrected for dead time, background, and half-life. A plot of $\log_{10}(C_{115m})$ versus x^2 showed the Gaussian behavior expected for volume diffusion, and the slope of this plot was very nearly identical to that for Cd^{109}.

D. Measurement of the Relative Activities of Cd^{109} and Cd^{115m}

Variation of the concentration ratio $C_a/C_b = C_{109}/C_{115m}$ from sample to sample may be inferred from the variation of the relative activity of the two iostopes among the respective solutions. Such a relative activity may be measured using any portion of the solutions. To eliminate inaccuracies arising from attenuation of radiation by the lead ions in the solutions, the lead was precipitated from solution in the form $PbSO_4$ by adding an appropriate quantity of Na_2SO_4 to each solution. After centrifuging, a portion of the remaining clear solution of each sample was evaporated within a central indentation on an aluminum planchet. Indentation of the planchets was performed so that the resultant residue of cadmium salt would be of similar geometry for all samples.

The β filter used for counting of the 22-keV x ray was a Plexiglas plate milled flat to a thickness of 0.296 ±0.002 in., and was placed between the sample and the detector. Energy discrimination was used to isolate the x-ray peak, the window being set from about 12–72 keV. In order to count the Cd^{115m} β radiation, the filter was removed and the window set from 225 keV to about 1.4 MeV. As may be seen in Fig. 4, the β spectrum, as seen by our equipment, is not the broad peak of the true energy distribution. The continuous increase of the counting rate with decreasing energy is due to backscattering out of the detector. A β may enter the detector and be scattered back out, leaving only part of its energy in the detector, so that many of the high-energy β rays appear lower in the spectrum than they should. An extremely stable high-voltage supply for the detector is then required to assure stability of the counting rate, since any small drift of the baseline at 225 keV results in a significant change in the counting rate.

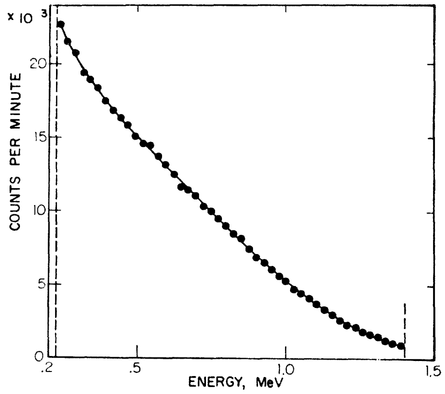

FIG. 4. β spectrum of Cd^{115m}, as detected and counted in this experiment.

Separate counting runs were conducted for the 22-keV x ray to measure C_{109}, and for the β radiation to measure C_{115m}. Prior to each counting run, the counting-rate stability, and reproducibility of data were tested. These tests were satisfactory and indicated that the measurements of C_{109} and C_{115m} should have an accuracy close to the statistics of counting. To verify the accuracy of final determinations of C_{109}/C_{115m}, samples were prepared to determine a zero-isotope effect. These samples were prepared from aliquots of the most active solution so as to be spread over a wide range in total activity, and were counted along with the other samples. The activities of all samples were measured relative to that of the first sample by counting this first sample both before and after every other sample. In this way it was possible to also maintain a check on both stability and reproducibility during the counting runs. A total of more than 10^6 counts of each isotope were collected from each sample. The question of how well each isotope was counted in the presence of the other is considered in the Appendix.

IV. RESULTS

The isotope effect is to be determined from the slope of the plot of $\ln(C_a/C_b)=\ln(C_{109}/C_{115m})$ versus $\ln(C_a)=\ln(C_{109})$, according to Eq. (4). The abscissa $[\ln(C_a)]_n$, of each data point n in Fig. 5 is taken from the measurement of the 88-keV γ ray previously described.

In order to calculate the ordinate values $[\ln(C_a/C_b)]_n$, the counting rates determined from measurement of the 22-keV x ray and of the β radiation were first corrected for background radiation and dead time. To correct for isotopic decay, it was noted that the total elapsed time of each counting run was small compared to the mean life τ of either isotope. For a counting period ΔT beginning at time T, the corrected counting rate is then

$$\left.\frac{dN}{dt}\right|_{t=0}=\left(\frac{N_{\text{tot}}-N_{\text{bkgd}}}{\Delta T-\Delta T_{\text{dead}}}\right)\left(1+\frac{1}{\tau}(T+\tfrac{1}{2}\Delta T)\right). \tag{7}$$

The counting rate of each isotope for each sample was then divided by the average counting rate of the preceding and following reference counts of the first sample. The effect of systematic drifts in the electronics is minimized in this way. The ordinate value for each sample n was then calculated from

$$\left[\ln\left(\frac{C_a}{C_b}\right)\right]_n=\ln\left(\frac{C_{a,n}/C_{a,1}}{C_{b,n}/C_{b,1}}\right), \tag{8}$$

so that the first sample has an ordinate of zero.

The error bars shown in Fig. 5 are ±0.002, and are derived solely from the counting statistics. Poisson statistics obtain for the four independent counting rates in the ratio

$$R_n=\frac{C_{a,n}/C_{a,1}}{C_{b,n}/C_{b,1}}. \tag{9}$$

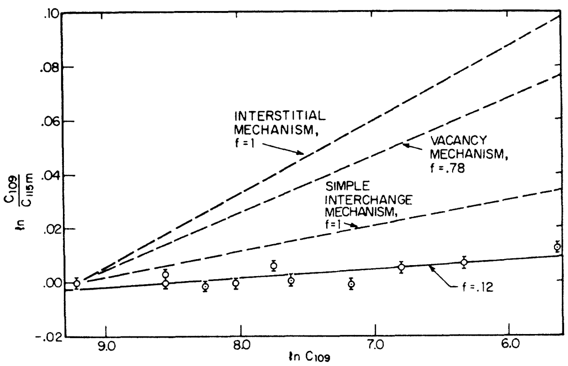

FIG. 5. Relative rates of diffusion of Cd^{109} and Cd^{115m} in pure lead at 248°C.

Since a total of approximately $n=10^6$ counts were collected for each measurement $C_{i,n}$,

$$\Delta C_{i,n}/C_{i,n}=(\sqrt{n})/n=0.001, \tag{10}$$

where $\Delta C_{i,n}$ is the standard deviation for each quantity $C_{i,n}$. The standard deviation of each ordinate value $[\ln(C_a/C_b)]_n=\ln(R_n)$ may then be obtained from

$$[\Delta\ln(R_n)]^2=\left(\frac{\Delta R_n}{R_n}\right)^2=\left(\frac{\Delta C_{a,n}}{C_{a,n}}\right)^2+\left(\frac{\Delta C_{a,1}}{C_{a,1}}\right)^2+\left(\frac{\Delta C_{b,n}}{C_{b,n}}\right)^2+\left(\frac{\Delta C_{b,1}}{C_{b,1}}\right)^2. \tag{11}$$

It follows that $\Delta\ln(R_n)=0.002$.

Using the method of least squares,[21] a straight line was fitted to the final data points in accordance with Eq. (4). The slope of this line, shown as a solid line in Fig. 5, is

$$-(D_a/D_b-1)=-0.0032\pm0.001, \tag{12}$$

where 0.001 is the estimated standard deviation. If the standard deviation of the ordinate values results from counting statistics alone, then $\chi^2=20$ for the 9 deg of freedom, with an associated probability of about 2%. This estimate of the ordinate standard deviation is probably a little too small, especially since counting of the β radiation is very sensitive to electronic stability. Such instabilities may increase the error for each point somewhat. The associated probability is increased to 5% if additional error increased the ordinate standard deviation to 0.0022, and to 50% if this standard deviation is increased to only 0.0031. It is thus considered that small additional incalculable errors, probably due to electronic instability, account for the large apparent value of χ^2. It should be noted that the estimated standard deviation of the slope does not depend in any way on the ordinate standard deviation if it is constant for all data points.

Uncertainties in the values of the abscissa $[\ln(C_a)]_n$ are much larger, of the order 1%, than those for the

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[21] J. R. Wolberg, *Prediction Analysis* (D. Van Nostrand Co., Inc., Princeton, N. J., 1967), Chap. 3.

ordinate. These errors enter into the least-squares determination in factors of the form $\sigma_y^2+(a\sigma_x)^2$, where σ_y and σ_x are the standard deviations for ordinate and abscissa, and a is the calculated slope. Since $|a|\simeq 0.003$, the effect of σ_x is negligible in this case.

A repetition of the counting procedures gave a slope of -0.0046 ± 0.002, in good agreement with the previous result (12). Scatter of the data for this run was much greater than for the first run, so that (12) is considered a more reliable determination of the isotope effect.

The accuracy of the experimental method was verified by the result of the zero-isotope-effect determination. The samples were all aliquots of the same solution, and covered a greater range in total activity than those for the diffusion isotope effect. The resultant slope was $+0.0004\pm 0.001$, or zero within the estimated standard deviation. Assuming again that the ordinate standard deviations result only from the counting statistics, $\chi^2=9.4$, with an associated probability somewhat greater than 5%. It is concluded that the equipment used for counting had no significant bias dependent on counting rate.

V. DISCUSSION

Since the penetration of both isotopes into the lead single-crystal specimen was shown to be the Gaussian penetration of the volume diffusion, the measured isotope effect 0.0032 ± 0.001 is that for the volume diffusion of cadmium in lead. The accuracy of this measurement of the isotope effect for diffusion has been tested and verified by separate determination of a zero-isotope effect. Precision in measurement of the values $[\ln(C_a/C_b)]_n$ was very close to that defined by the statistics of counting; the small additional experimental error was probably due to the effect of electronic instability, principally in counting the Cd^{115m} β radiation. In future measurements of this type, it may be possible to minimize error due to electronic drift by the use of a solid-state detector. This detector is essentially drift-free and has a much greater resolution, so that energy discrimination may be used with greater precision.

The interstitial and simple vacancy mechanisms involve single atomic jumps, so that $n=1$ in Eq. (2). Assuming that $\Delta K=1$ and substituting the result of Eq. (2) and the experimentally determined isotope effect (12) into Eq. (1), the correlation factor for solute diffusion by either of these mechanisms is calculated to be $f=0.12\pm 0.03$.

Such a small correlation factor is clearly inconsistent with solute diffusion by the interstitial mechanism, for which $f=1$. It is anticipated that the correlation factor for rapid solute diffusion by the simple vacancy mechanism should be less than that for self-diffusion, i.e., $f<f_0=0.78146$,[22] so that the experimental result is, of itself, in agreement with solute diffusion by the vacancy mechanism. It has been demonstrated, however, that the linear enhancement of self-diffusion by additions of cadmium is much too small for such fast diffusion by the vacancy mechanism.[11]

Disagreement with the simple vacancy mechanism for the diffusion of cadmium in lead may be further substantiated by determining the minimum linear-enhancement factor consistent with the solute correlation factor determined by this experiment, $f=0.12$, and the solute to self-diffusivity ratio at the same temperature.[11] These two results are used to determine the locus of all consistent sets of the three jump-frequency ratios in the tables of Howard and Manning.[23] The minimum linear-enhancement factor calculable along this locus is approximately $b_{11}=62$. Since the observed linear-enhancement factor at this temperature, $b_{11}=30$, is much smaller than this minimum, we conclude that cadmium does not diffuse in lead by the simple vacancy mechanism.

It has been mentioned that the temperature dependence of the linear-enhancement factor for self-diffusion b_{11} agrees very closely with Eq. (5), which is also the relation between solute and self-diffusion expected for the simple interchange mechanism of solute diffusion. Since this mechanism envisions the simultaneous jump of two atoms so as to interchange positions, $n=2$ in Eq. (2). The correlation factor for solute diffusion then calculated from the isotope effect is $f=0.36$. Since solute diffusion by this mechanism is uncorrelated, so that $f=1$, the observed isotope effect is much too small to be consistent with this mechanism.

The isotope effect measured for the diffusion of cadmium in lead is one of the smallest measured for diffusion in crystalline solids. Such a small effect agrees reasonably well with ring mechanisms involving the simultaneous jumps of two or three solvent atoms and a solute atom. One would expect the activation energy for such a process to be very high, however. In addition, the linear-enhancement factor b_{11} for additions of solute diffusing by such mechanisms must be two or three times the ratio D_2^0/D_1^0, much larger than the observed enhancement effect.[11] It is, therefore, concluded that cadmium does not diffuse in lead by such a ring mechanism.

We have thus demonstrated that the diffusion of cadmium in lead, as characterized by measurements of the isotope effect, the solute to self-diffusivity ratio,[11] and the linear enhancement of self-diffusion,[11] is inconsistent with the interstitial, vacancy, simple interchange, and ring mechanisms.

Since the proposed interstitial-vacancy pair mechanism[15] involves single atomic jumps, the correlation factor $f\cong 0.12$. The model for solute diffusion by this mechanism[15] has predicted that the solute correlation factor must be very small, and the experimental result confirms this expectation. As the observed linear

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[22] K. Compaan and Y. Haven, Trans. Faraday Soc. **52**, 786 (1956).

[23] R. E. Howard and J. R. Manning, Phys. Rev. **154**, 561 (1966).

enhancement of self-diffusion is also best explained on the basis of interstitial-vacancy pair defects, it is concluded that cadmium solute diffuses in lead primarily by means of the interstitial-vacancy pair mechanism. It is thus implied that cadmium dissolves in lead both substitutionally and interstitially,[15] but that the interstitial solute ions are strongly attracted to vacancies. This attraction leads to a significant fraction of interstitial solute-vacancy pairs, and the migration of associated interstitial solute ions is highly correlated due to migration of the associated vacancies.

Many independent experiments[24] evidence the tendency for metallic solutes of small valence to dissolve interstitially in polyvalent metals. In order to under-understand the effect of solute valence on interstitial-substitutional equilibrium, the valence dependency of the energy terms which determine this equilibrium have been examined.[20,25] An increased tendency for interstitial dissolution was predicted in those alloys for which the solvent valence is large and the solute valence small, in agreement with the experimental observations. It is, therefore, not surprising that cadmium should dissolve at least partially in the interstices of lead, in much the same manner as the noble-metal solutes.[13,14]

The association of interstitial cadmium ions and vacancies may be understood on the basis of a screened electrostatic interaction. It may be assumed, lacking evidence to the contrary, that solute atoms in a metallic solvent contribute all electrons outside the last closed shell to the conduction band of the alloy. Solute-vacancy interactions and the reslutant solute diffusivity in substitutional solutions in silver, copper, and zinc have been explained by a screened electrostatic interaction between the effective charge of the solute ion and the negatively charged vacancy.[26,27] March and Murray[28] have recently calculated self-consistently the electronic potential for a free-electron gas into which a point charge, representing an impurity ion, has been introduced. The results indicate that the electrostatic interaction between impurity ion and vacancy is screened out at somewhat greater than nearest-neighbor distance for solvents such as silver, copper, and zinc, so that consideration of only nearest-neighbor interactions is a good approximation. For polyvalent solvent metals such as aluminum and lead, however, the interaction may be completely screened at the nearest-neighbor distance, and substitutional solute-vacancy interaction may thus be negligible. Peterson and Rothman[29] have found that the diffusivities in aluminum of many impurities of very different valences are very nearly equal, suggesting that the screened electrostatic solute-vacancy interaction in aluminum is very small. Data for the diffusivity of thallium in lead[30] suggest that the same may be true for substitutional solutes in lead.

If cadmium were substitutionally dissolved in lead, and diffused by the simple vacancy mechanism, we would expect the solute-vacancy interaction to be repulsive, and the solute diffusivity, therefore, slow. We suggest, however, that substitutional cadmium, like the solute thallium, interacts only weakly with vacancies, so that the resultant diffusivity of substitutional cadmium is nearly that of lead self-diffusion. An interstitial cadmium-ion nearest neighbor to a vacancy, however, interacts at a shorter range than the screening radius with an effective positive charge, so that an appreciable binding energy may result. It is thus understandable, on the basis of screened electrostatic interactions, that a significant fraction of interstitial cadmium-vacancy pair defects are formed in the cadmium-lead alloy.

We may also expect the monovalent noble-metal solutes to display an even greater tendency to dissolve interstitially in lead than does cadmium, by virtue of their smaller valence. In addition, these solutes should interact more weakly with vacancies, so that the fraction of free interstitial solute atoms is further enhanced. The ultrafast diffusion of these solutes in lead, and the lack of an observable enhancement of the self-diffusion[13] are evidence that this is the case.

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APPENDIX: SEPARABILITY OF THE ISOTOPES

As mentioned in the Introduction, it is important to ascertain how well the two isotopes may be separately counted in the presence of each other.

The highest-energy radiation from the decay of Cd^{109} is the 88-keV γ ray. Therefore, there should be no

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interference from the Cd^{109} in counting of the Cd^{115m} 1.63-MeV β ray if the base line discriminator of the single-channel analyzer is set at a sufficiently high energy. This baseline was set at about 225 keV. A very generous upper limit for possible interference was determined by counting a sample with the window set for counting the β radiation, but using the β-ray filter. This count rate was approximately 0.8% of the count rate in the absence of the filter.

We may estimate an upper limit for the contribution of the Cd^{115m} radiation to the count rate of Cd^{109} by considering the scattering probability for the high-energy γ ray in the decay scheme of Cd^{115m} (see Fig. 1). For our $\frac{1}{4}$-in. NaI crystal, we obtain[19] 0.5% as an upper limit for the fraction of Cd^{115m} counts which result in a γ ray that interacts with the detector.

Another undesirable contribution to the counting of Cd^{109} results from ionization of the innermost electron of Cd^{115m} by the 1.63-MeV β ray. This is followed by a K x ray in the vicinity of 20 keV. The probability for this process[31] is $0.64/Z^2$. For Cd, $Z=48$, and the fractional occurrence is 0.023%.

We must finally estimate the result of crossover effects on the measurements of the ratio C_a/C_b. Because of crossover effects, we experimentally measure the ratio

$$R=(C_a+e_1C_b)/(C_b+e_2C_a)\,, \qquad (13)$$

where e_1 is the fraction of C_b contributing to measurement of the count rate C_a, and e_2 the fraction of C_a contributing to C_b. We are attempting to measure a small change in C_a/C_b from sample to sample, and therefore, wish to know how accurately changes in the measurements of R reflect the actual changes in C_a/C_b. This is a question of functional dependence, and not of counting statistics. Assuming that the e_i are small, and $C_a/C_b\sim 1$,

$$R\simeq C_a/C_b+e_1-e_2(C_a/C_b)^2\,, \qquad (14)$$

$$\delta R\simeq \delta(C_a/C_b)[1-2e_2(C_a/C_b)]\,. \qquad (15)$$

The e_i are at most about 1%, and the ratio of the actual count rates $C_a/C_b\simeq 2$, so that $\delta R=\delta(C_a/C_b)$ to within about 4%. This implies that the measured solpe of $\ln(R)$ versus $\ln(C_a)$ is equal to the actual slope of $\ln(C_a/C_b)$ versus $\ln(C_a)$ to within 4%. Since the estimated standard deviation of the final result for the slope is about 30% of the determined value, the effect of crossover on the accuracy of the final result is negligible.

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Slowly Diffusing Impurities in Lithium Metal

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The diffusion of Sn, Pb, Sb, and Bi tracers in Li metal has been investigated, using a thin-film evaporating-sectioning technique. The results can be expressed by the Arrhenius relations $D_{\rm Sn}=0.62\ e^{-(15.0\pm1.2)/RT}$, $D_{\rm Pb}=1.6\times10^2\ e^{-(25.2\pm1.2)/RT}$, $D_{\rm Sb}=1.6\times10^{10}\ e^{-(41.5\pm4.5)/RT}$, and $D_{\rm Bi}=5.3\times10^{13}\ e^{-(47.3\pm3.4)/RT}$. The data are not in agreement with established diffusion models based on attractions between vacancies and excess valency ions. Instead, diffusivity appears to decrease as the valency of the impurity increases. However, on the assumption that it is not probable for an impurity in a highly electropositive matrix to be more than singly ionized, the diffusive behavior of impurities in Li can be at least qualitatively understood in terms of two competing mechanisms, to the effect that relatively large and electropositive impurities should diffuse mainly via vacancies, small and electronegative impurities as interstitials.

INTRODUCTION

DURING recent years a systematic study of atom transport in solid and liquid alkali metals has been pursued at Gothenburg. The main interest has been concentrated on lithium. This metal, possessing a particularly simple electronic structure and extremely low atomic mass, is rewarding from the point of view of experiments as well as theory. The phenomena hitherto studied in solid Li include thermomigration,[1,2]

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