

Diffusion of copper in lead: Solubility and isotope effect*

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The solubility of copper in lead has been measured by a diffusion technique and found to be $\approx 4 \times 10^{-4}$ wt% at 321.3°C, which is an order of magnitude lower than the accepted value. This low solubility may be responsible for the scatter of the data on the diffusion of copper in lead. The isotope effect for the diffusion of copper in lead has been measured by the half-life separation technique. The result, 0.23 ± 0.08 , is close to the value for the diffusion of silver in lead and much less than the value expected for a simple interstitial.

I. INTRODUCTION

The diffusion of noble metals in lead has been studied longer and more frequently than impurity diffusion in any other host metal.¹⁻¹² These studies have shown that copper, silver, and gold diffuse much more rapidly in lead than is common for impurity diffusion in most host metals. The characteristics of this type of fast impurity diffusion are: the activation energy Q_I and preexponential factor $(D_0)_I$ for impurity diffusion are significantly lower than the activation energy Q_H and preexponential factor $(D_0)_H$ for self-diffusion in the host lattice; the activation volume for impurity diffusion ΔV_I is less than one-half the atomic volume of the host lattice V . Values of these characteristics for the noble metals diffusing in lead are given in Table I.

The characteristics shown in Table I have led to the interpretation that noble metals diffuse and dissolve interstitially in lead, and, finally, to the proposal that diffusion occurs by means of the dissociative mechanism.¹³ This mechanism involves an equilibrium between substitutional solute atoms (concentration C_s) and interstitial solute atoms (concentration C_i). If D_i and D_s are the respective coefficients of the interstitial and substitutional atoms, then the solute diffusivity is given by

$$D_I = \frac{C_i}{C_i + C_s} D_i + \frac{C_s}{C_i + C_s} D_s, \quad (1)$$

and it is thought that $D_i \gg D_s$. The large differences in the diffusion coefficients of the various noble metals in lead have been explained^{9,14} in terms of the large differences in their C_i/C_s ratios. The particularly low values of Q_I/Q_H and $\Delta V_I/V$ found for the copper/lead system have been interpreted^{9,12} as showing that copper dissolves and diffused largely on interstitial sites. The larger values of Q_I/Q_H and $\Delta V_I/V$ found for the gold/lead and silver/lead systems then suggest an increasing amount of diffusion by means of the substitutional mechanism.

The presence of two mechanisms of diffusion could lead to curvature in the Arrhenius plots and

also the $\ln D$ versus pressure plots. Evidence on this point is conflicting. The Arrhenius plots for both the gold/lead^{6,8} and silver/lead⁹ systems show no curvature. The $\ln D$ versus pressure plots show no measurable curvature for either the silver/lead or gold/lead systems, according to Weyland *et al.*¹¹ However, measurements of the effect of pressure on diffusion in the gold/lead and copper/lead systems by Ascoli *et al.*^{15,16} have shown evidence of two mechanisms in both systems. The latter results suggests that the previous interpretation^{9,12} that $C_i/(C_i + C_s)$ was close to unity for Cu in Pb is not valid.

Recent studies of precipitation¹⁷ and diffusion¹⁸ in the gold/lead system have suggested that although a dissociative mechanism may be a good description of the diffusive process, neither of the defects involved in this mechanism is a simple interstitial. The particular model that best explains the precipitation and diffusion studies is a split interstitial model. Studies of internal friction¹⁹ and superconductivity²⁰ of dilute gold/lead alloys have also suggested a split interstitial model. (In the superconductivity work, the term di-interstitial was used since it indicates that no solvent atom is involved in the defect.) Thus the details of the atomic mechanism of diffusion of noble metals in lead are still not clear. We have chosen to measure the isotope effect in diffusion because of the value such measurements have provided in the determination of diffusion mechanisms.

The relationship between the isotope effect and the diffusion mechanism comes in through the correlation factor, via the equation^{21,22}

$$\frac{D_\alpha}{D_\beta} - 1 = f \Delta K \left[\left(\frac{m_\beta}{m_\alpha} \right)^{1/2} - 1 \right]. \quad (2)$$

Here D_α , m_α and D_β , m_β are the diffusion coefficients and masses of the isotopes α and β , f is the correlation factor, and ΔK is the so-called kinetic-energy factor.^{22,23} When the diffusion process is the result of more than one mechanism, Eq. (2) becomes

TABLE I. Diffusion parameters for noble-metal diffusion in lead.

Impurity	Host	Q_I/Q_H	$(D_0)_I/(D_0)_H$	Ref.	$\Delta V_I/V$	Ref.
Cu	Pb	0.31	8×10^{-3}	9, 13	0.04	12
Au	Pb	0.39	9×10^{-3}	8, 13	0.28	11
Ag	Pb	0.56	5×10^{-2}	9, 13	0.34	11

$$\left(\frac{D_\alpha}{D_\beta} - 1\right) = \sum_i p_i f_i \Delta K_i \delta m_i, \quad (3)$$

where the subscript i refers to the i th mechanism, and p_i is the fraction of the diffusion occurring by that i th mechanism. The term δm_i is a generalized mass term, which is a function of the masses of all atoms involved in the jump process. This equation has been used to analyze the unexpectedly low value of the isotope measured for the diffusion of silver in lead.²⁴ The analysis showed that (a) the substitutional component of the diffusion process was not large, and (b) the interstitial component could not be explained in terms of a simple interstitial mechanism. The term simple interstitial mechanism as used here means a single interstitial diffusing by random motion through the lattice with a value of ΔK close to unity.

The present measurements of the isotope effect for the diffusion of copper in lead were made as a check of the low isotope effect found for the Ag/Pb²⁴ system and as an attempt to obtain further information on the nature of the defect responsible for fast impurity diffusion.

The experimental measurements are difficult because the low solubility of copper in lead²⁵ can cause the time required for the dissolution of the copper isotope layer to be comparable with the anneal time.⁸ The analyses of this problem^{8,26} indicated that special care had to be used in the experiment to ensure that the low solubility would not affect the diffusion measurement.

The method most frequently used for the accurate determination of diffusion coefficients is the deposition of a thin layer of radiotracer onto one end of a sample followed by annealing, sectioning, and counting of the sections. The method usually results in a Gaussian depth dependence of the concentration, i. e.,

$$c(x, t) = [M/(\pi Dt)^{1/2}] e^{-x^2/4Dt}. \quad (4)$$

Here $c(x)$ is the concentration of tracer as a function of the depth x , M is the amount of copper deposited on the surface of the sample, D is the diffusion coefficient, and t is the annealing time. Accurate measurements of the diffusion coefficients and mass effects are possible only when the experimentally obtained concentration profiles are Gaussian. Dyson *et al.*⁹ noted that Gaussian profiles do not result when oxidation of the lead surface occurs

at the Cu/Pb interface. (The problem of oxidation of the radioisotope has been discussed by Hales.²⁷) Also, Gaussian profiles are not found when the thin layer of radiotracer has insufficient time to dissolve during the course of the anneal owing to the low solubility of the tracer in the host metal.

When the time required for the thin layer to dissolve, τ , is less than the anneal time, t , the concentration follows the equation²⁶

$$c(x, t) = \frac{2c_0}{\pi^{1/2}} \int_{x/\sqrt{2Dt}}^{\infty} e^{-y^2} \operatorname{erf}\left[y\left(\frac{\tau}{t-\tau}\right)^{1/2}\right] dy, \quad (5)$$

where c_0 is the solubility of copper in lead.

This profile diverges from a Gaussian (Fig. 1) until the anneal time becomes four or five times greater than the dissolution time. The curves then approach a Gaussian, but with an incorrect value of D . Figure 1 also shows that if the penetration is not followed more than one order of magnitude in the specific activity, the deviation of the points from a straight line will be extremely difficult to observe. This is particularly true in the copper/lead system where the strong absorption of the copper activity by lead can cause significant scatter due to shifting of the sections in the counting bottles. The scatter could mask curvature in a penetration plot, leading to an erroneous value of D . This effect could be responsible for some of the scatter in the data on the diffusion of Cu in Pb, because the values of τ/t are large. The value of τ is large because C_0 is small^{8,26}; the value of t

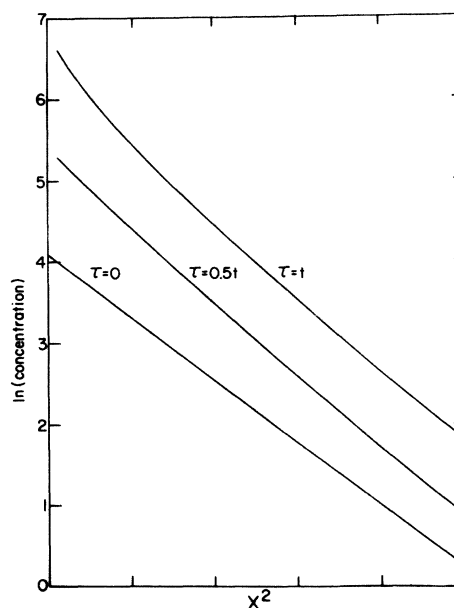


FIG. 1. Penetration profiles as a function of the ratio of τ/t (the time for the solute to dissolve/the diffusion anneal time).

cannot be increased to compensate for this because of the limitations of a practical sample size combined with the large value of D . The problem of solubility is thus closely connected to the measurement of the isotope effect.

II. EXPERIMENTAL METHODS

A. Materials

Single crystals of lead were grown in quartz tubes from the melt of 99.9999%-pure lead obtained from Cominco American, Inc. The cylindrical crystals were 1 in. in diameter and were spark cut normal to the cylindrical axis to provide samples $\frac{1}{2}$ in. thick. The radiotracer used for the preliminary studies of oxidation and solubility was ^{64}Cu obtained from irradiation of pure copper (99.9999%) foil in the Argonne CP-5 reactor. For the measurement of the isotope effect in diffusion, the isotopes ^{67}Cu and ^{64}Cu of much higher specific activity were obtained from Oak Ridge National Laboratory. They were made by fast-neutron irradiation of ZnO enriched in ^{67}Zn and ^{64}Zn , respectively, and subsequently chemically separated, but were not carrier free because of the copper impurity present in the ZnO starting material. The specific activity of both isotopes at the time of the diffusion anneal was on the order of 500 Ci/(g Cu).

B. Isotope deposition and diffusion annealing-avoidance of oxidation

The high count rates required for measurements of the isotope effect in diffusion together with the low solubility of copper in lead demanded a reliable and reproducible technique for the deposition of the radiotracer. The chemideposition and electroplating techniques, when conducted in a normal laboratory atmosphere,^{9,12,16} were found to be irreproducible. The problem was solved by working in a dry box with a flowing argon atmosphere (< 50 ppm H_2O). The lead surface was cleaned by taking a thin slice with a microtome. The chemideposition of the copper radiotracer was started immediately by placing a small volume (~0.4 ml) of the copper salt dissolved in water on the end of the 1-in.-diam samples. The fraction of the isotope that plated out as a function of time and under the prescribed conditions was reproducible, as can be seen from Fig. 2. For the isotope-effect measurement, the radiotracers ^{67}Cu and ^{64}Cu were chemideposited onto a clean lead surface as described above. The activity of ^{64}Cu was approximately six times greater than that of the ^{67}Cu at the time of the diffusion anneal.

After chemideposition the samples were placed in a small gas-tight aluminum capsule and transferred outside the dry box for anneal in a molten salt bath. The bath was controlled to $\pm 0.1^\circ\text{C}$, and

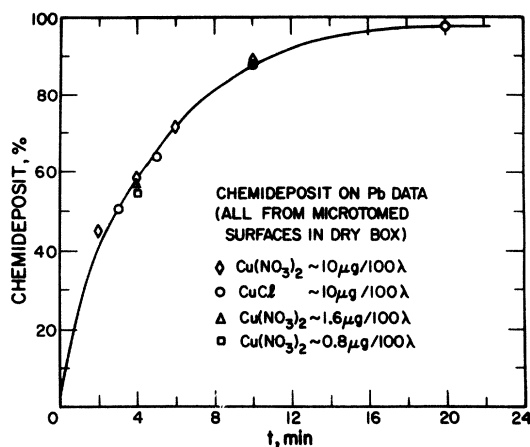


FIG. 2. Plot of efficiency of chemideposition as a function of time.

the temperature of the sample was followed continuously with a copper-constantan thermocouple. The capsule was quenched in water at the end of the anneal. The combination of a small aluminum capsule and a molten salt bath was used to allow fast heat up and quench times and in this manner define as closely as possible the short anneal times that the high diffusion rates make necessary. The error of 2–3% in our anneal time was the largest error in our measurement of D . Test anneals of the samples prepared in the manner described above showed that the effects of oxidation were minimized. A test diffusion anneal was also made to obtain a value of the solubility at a temperature of 323°C . The ^{64}Cu had a specific activity of 6 $\mu\text{Ci}/\mu\text{g}$ at the time of the diffusion anneal, and 30 μg of copper was deposited as a thin layer on an area of 4 cm^2 . The sample was annealed for 15 min at 321°C and then quenched and sectioned.

C. Sectioning and counting

After the anneal, the samples were quenched and their diameters reduced by machining to eliminate the effects of surface diffusion. The samples were aligned in a microtome so that cuts were taken parallel to the original microtomed surface. Each section (~250 μm) was comprised of many slices (~50), which was placed in a tared counting vial. These sections were then dissolved, after weighing, in equal volumes of an acetic acid-hydrogen peroxide (2:1 by volume) solution.

The concentration of radioactive copper was determined in each section using a NaI(Tl) counting apparatus. The depth dependence of the concentration was calculated from the measured diameter of the samples, weights of the sections, and the density of lead. The measured count rates of ^{67}Cu were dependent on the quantity of lead present in the counting vials. This dependency made the ratio

of $^{67}\text{Cu}/^{64}\text{Cu}$ quite sensitive to the lead content, as can be seen from the scattered results of a preliminary experiment in Fig. 3. For this reason, the lead was removed by the addition of a saturated solution of sodium sulfate and centrifuging to remove the precipitate.

The counting procedures used to differentiate between the ^{67}Cu and ^{64}Cu isotopes in each section followed closely those used by Rothman and Peterson.²⁸ Each section was counted at least ten times over a 3-day interval each time to 10^6 counts. The ratios of $^{67}\text{Cu}/^{64}\text{Cu}$ were determined by fitting the counting data to the time t elapsed since an arbitrary time zero

$$A = C_{64} e^{-\lambda_{64}t} + C_{67} e^{-\lambda_{67}t}, \quad (6)$$

where C_{64} and C_{67} are the specific activities of ^{64}Cu and ^{67}Cu at time zero, and λ_{64} and λ_{67} are their decay constants. The count rates were corrected for counter background and dead time. The procedure for removal of the lead by precipitation proved unusually time consuming; therefore, the procedure of diluting all high count-rate sections to an initial count of 5×10^5 counts/min was not followed in this work.

III. EXPERIMENTAL RESULTS

A. Solubility

The concentration profile obtained in this experiment is shown in Fig. 4. The initial dip in the concentration profile is attributed to out diffusion of copper during the quench.²⁹ Extrapolation of the curve back to the ordinate allows one to estimate the solubility of copper in lead as $\sim 4 \times 10^{-4}$ wt% copper at 321°C . Similar analysis of penetration profiles in Candland's thesis³⁰ yields values of 2.8×10^{-4} wt% (286°C) and 2.6×10^{-4} wt% (271°C).

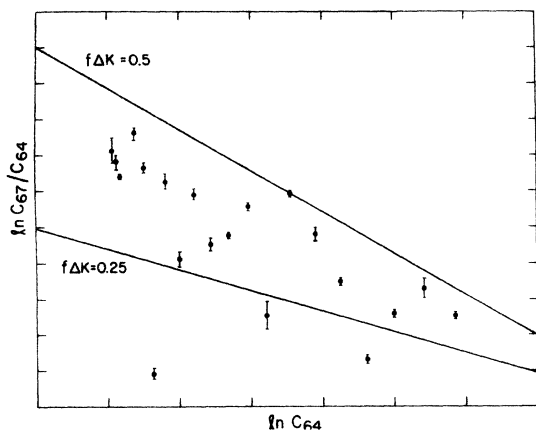


FIG. 3. Diffusion of ^{67}Cu and ^{64}Cu in lead at 227.9°C . Each division on the ordinate is 0.01 and each division on the abscissa is 1.0.

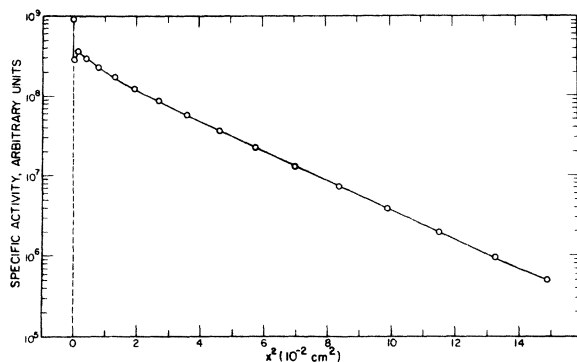


FIG. 4. Penetration profile for ^{64}Cu diffusing in lead at 323°C .

B. Isotope effect

The concentration profiles obtained for the isotope-effect experiments are shown in Fig. 5. The lower line was obtained for a sample annealed at 318.8°C and with the ^{67}Cu and ^{64}Cu isotopes mixed prior to deposition. The upper line was obtained for a sample annealed at 321.6°C and with the isotopes deposited on separate areas of the lead surface that were separated by a distance greater than $3(Dt)^{1/2}$. The separate isotopic deposition experiment was an attempt to investigate the possibility of two-atom diffusion mechanisms. The concentration dependence of the total activity of ^{67}Cu and ^{64}Cu is shown in Fig. 5 and is Gaussian over a drop of four orders of magnitude in activity. The diffusion coefficients obtained from these profiles are $(8.14 \pm 0.20) \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ (318.8°C) and $(8.69$

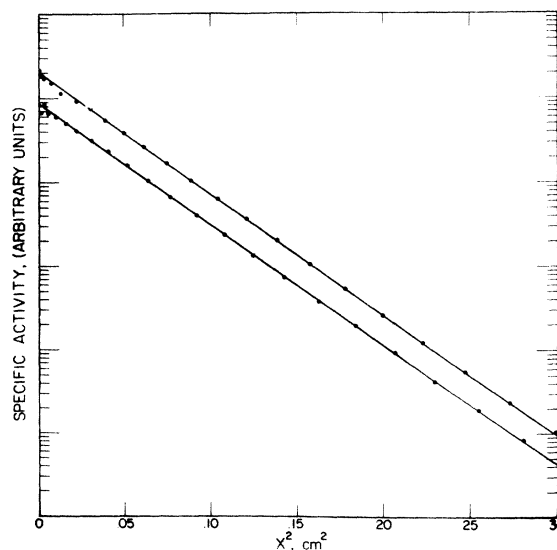


FIG. 5. Penetration profiles for $^{67}\text{Cu} + ^{64}\text{Cu}$ diffusing in lead. Upper line is for anneal at 321.6°C , and lower line is for anneal at 318.8°C .

$\pm 0.20) \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ (321.6 °C). Use of Eq. (6) allowed concentration profiles of the individual isotopes to be obtained. The analysis of these profiles showed that a certain amount of hold up of the ^{64}Cu isotope had occurred in the 321.6 °C sample. Although the small change in the measured diffusion coefficient as a result of the hold up was within the experimental error, it was sufficient to completely nullify the effect of mass on the diffusion coefficient.

The value of the isotope effect [Eq. (2)] for the 318.8 °C anneal was obtained using the equation³¹

$$\ln(C_{87}/C_{64}) = \text{const} - \ln C_{87}(D_{87}/D_{64} - 1). \quad (7)$$

A plot of $\ln(C_{87}/C_{64})$ vs $\ln C_{87}$ is shown in Fig. 6 for three values of the counter dead time, τ_d . Evidently the value of $\ln(C_{87}/C_{64})$ is sensitive to the value of τ_d used in the calculation for count rates above 8×10^5 counts/min. This sensitivity is the reason for diluting hot sections to count rates of about 5×10^5 counts/min, a step that was omitted in this experiment as mentioned in Sec. II C. At high count rates, the dead time was found to be count-rate dependent. A count-rate-dependent dead time measured by the two-source method also gave a curvature above 8×10^5 counts/min. We have therefore used only the points below this activity and obtained $1 - D_{87}/D_{64} = 0.0053 \pm 0.0015$, which is equivalent to an isotope effect of 0.23 ± 0.08 . The preliminary experiment (Fig. 3) also shows an isotope effect of less than 0.5.

IV. DISCUSSION

Two important points can be seen from the experimental measurements. The solubility of copper in lead is considerably lower than previously reported,³² and the isotope effect for the diffusion of copper in lead is small. The solubility of copper in lead has frequently been quoted as 7×10^{-3} wt%.^{9,12,25} This would appear to be the figure quoted by Hansen.³² The original reference³³ suggests the solubility is considerably lower than this value. Our value, $\sim 4 \times 10^{-4}$ wt%, is about a factor of 20 lower than the previously accepted value.

The low solubility of copper in lead has a number of consequences. The low solubility could account for the discrepancy between the activation energy for the diffusion of Cu in Pb determined by Candland *et al.*¹² (5.6 ± 0.5 kcal/mole) and Dyson *et al.*⁹ (8.0 ± 0.4 kcal/mole). Solubility is a more serious problem for the former than for the latter because the areas of the samples used by Candland *et al.* were much smaller. The curved penetration profiles observed in Candland's initial studies could have been largely the result of low solubility and not entirely due to surface oxidation of the lead. The values of the diffusion coefficient measured at ambient pressure for samples annealed with and

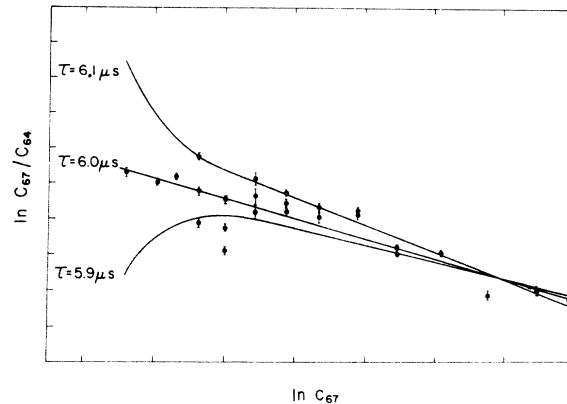


FIG. 6. Diffusion of ^{67}Cu and ^{64}Cu in lead at 318.8 °C. Each division on the ordinate is 0.01, and each division on the abscissa is 1.0.

without steps to prevent oxidation, which also helped to eliminate the solubility problem, are given in Candland's thesis.³⁰ A least-squares analysis of all diffusion coefficients measured at ambient pressure yields an activation energy of 5.8 ± 0.7 kcal/mole. The fit of only those values obtained with their improved techniques yields an Arrhenius equation

$$D = 2.6 \times 10^{-3} e^{(-7.0 \pm 0.5) / RT}. \quad (8)$$

The value of D calculated from Eq. (8) for 318.8 °C is 15% lower than our measured value. The value of D calculated from the Arrhenius equation determined by Dyson *et al.*⁹ agrees with the present work within experimental error. The lower values of D measured by Candland *et al.*¹² could be accounted for by the low solubility of copper in lead.

The above analysis indicates that the inclusion of data affected by solubility problems changes the values of D_0 by a factor of 3 and of Q by 25%. These changes would indicate that the abrupt change in values of D_0 and Q with increasing pressure found by Ascoli *et al.*¹⁶ may have arisen from solubility problems. The thickness of their copper deposits was some hundreds of atomic layers. Such thicknesses of copper would require tens of hours to dissolve even at the melting temperature. The penetration profiles shown in the work of Ascoli *et al.* are not followed for more than a one order of magnitude drop in activity so it is difficult to ascertain whether the profiles show curvature.

The other transport study of copper in lead is the thermomigration work of Sullivan *et al.*³⁴ In this work the samples were quenched in liquid nitrogen between the anneal and analysis. During the quench to liquid-nitrogen temperature, the low solubility would cause the copper to redistribute as much as possible to outside surfaces. It is impossible to determine the effect of low solubility on the mea-

sured value of Q^* .

The measured low value of $f\Delta K$ is close to the values of $f\Delta K$ found for the diffusion of silver in lead.²⁴ Since the mechanism of the diffusion of copper is thought to be the same as that of silver in lead, our value of the isotope effect for the diffusion of copper in lead supports the result of Miller *et al.*²⁴ for silver in lead, 0.25, as opposed to the value of 1.0 obtained by Herzig *et al.*³⁵

V. CONCLUSIONS

(1) The solid solubility of copper in lead near the melting point is about 4×10^{-4} wt%, an order of magnitude lower than the previously accepted value.

Such a low solubility can cause serious difficulties in the measurement of the impurity diffusion coefficient.

(2) The isotope effect for the diffusion of copper in lead is approximately 0.25 and is much lower than the value expected for a simple interstitial mechanism.

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