and so in preference de Launay's tables should always be used to obtain Θ(elastic) for cubic crystals.

CONCLUSION

Revised values of Θ_0 and Θ(elastic) for the three salts mentioned in the Rice Institute papers are given in Table I. [Θ(elastic) for LiF has been obtained from the elastic constants of Briscoe and Squire[15] using de Launay's tables. The value of 743° quoted in reference 7 was derived from their preliminary results.[16]] It will be seen that if Θ_0 is derived by extrapolating smoothly a graph of C_v/T^3 against T^2, then for each salt Θ_0 and Θ(elastic) agree well within the limits of experimental accuracy; there is no indication that $\Theta(\text{elastic})>\Theta_0$ (as suggested by Ludwig's calculations), although the limits of accuracy would in fact permit a difference of up to 1%. On the other hand, if Scales's values of Θ_0 for KI and LiF are chosen, we find that $\Theta(\text{elastic})>\Theta_0$ by about 2%.

The example of LiF is of particular interest because the lower estimate of Θ_0(722°K) is quoted by Ludwig (p. 300 of reference 3) as providing some confirmation for his theory; but as we have seen, measurements in the important range of temperatures below 20°K disagree. The resolution of this uncertainty by experiments of more reliable accuracy would be very desirable, since it would firmly settle both the shape of the C_v/T^3 curve (relevant to the harmonic theory) and the difference between Θ_0 and Θ(elastic)[17] (relevant to the anharmonic theory).

TABLE I. Characteristic temperatures at 0°K for KCl, KI, and LiF.

	KCl	KI	LiF
Θ(elastic)	236 ±1	131 ±2	735±5
Θ_0(extrapolated)	235.1±0.5[b]	132.3±1[b]	743±7[c]
Θ_0(Scales[a])	···	128.3	722±6

[a] See reference 2.
[b] See reference 8.
[c] See reference 7.

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[15] C. V. Briscoe and C. F. Squire, Phys. Rev. **106**, 1175 (1957).

[16] C. V. Briscoe and C. F. Squire, Bull. Am. Phys. Soc. Ser. II, 2, 18 (1957).

[17] It should be noted that Ludwig[3] finds that the classical relation between elastic constants and sound velocities is no longer strictly valid for longitudinal waves. If so, the values of c_{11} and c_{12} given by the pulse technique may not be exactly equal to the static values; however, no numerical estimate is given of the magnitude of this effect. Fortunately, Θ(elastic) depends mainly upon c_{44}, which is determined solely from the velocity of transverse waves.

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Diffusion Measurements in the System Cu-Au by Elastic Scattering

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A broad-range magnetic spectrograph has been used to study the diffusion of gold into copper in the temperature range 360–500°C by elastic scattering of protons and deuterons. This is a new technique in solid diffusion measurements and should have fairly wide applicability in intermetallic diffusion. This investigation extends the data a factor of 10^6 below the sectioning range. These results together with data of sectioning observers, show the Arrhenius law to be approximately valid over a range in D of 5×10^8. A precise fit to all the data requires a slight upward curvature. In the temperature range studied here, we obtain $Q=45,\,750\pm750$ cal/mole and $D_0=0.104\pm0.06$ cm²/sec. This represents a decrease of about 4000 cal/mole from the most precise data in the sectioning range. This curvature is attributed to diffusion along internal surfaces, although the possibility of multiple diffusion mechanisms still remains.

INTRODUCTION

ALTHOUGH considerable effort has been brought to bear on the problem of solid diffusion measurement and many ingenious methods have been used, the sectioning technique has become more or less standard because of its precision and wide applicability in metallic systems. However, because the depth of investigation ($\approx$0.01 cm) is so large, the method is effectively limited to the range of $D>10^{-12}$ cm²/sec. This, coupled with the upper limit imposed by melting point, has effectively limited the range of data to a few orders of magnitude in many cases. Nowick[1] and many others have pointed out the seriousness, for theoretical purposes, of the lack of sufficiently accurate data over sufficiently wide range. Methods extending the range significantly below 10^{-12} cm²/sec have been either indirect or else limited to specific systems having unique properties.[2–5] Extension of the data to low temperatures is of importance not only for increased accuracy, but also to explore for possible deviations from the Arrhenius law, indicating multiple mechanisms of diffusion, such as the suggestion of Lazarus of the possibility of barrier penetration in

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[1] A. S. Nowick, J. Appl. Phys. **22**, 1182 (1951).

[2] G. von Hevesy and W. Seith, Z. Physik **56**, 790 (1929).

[3] E. Cremer, Z. Physik Chem. **B39**, 445 (1938).

[4] W. Jost, Z. Physik Chem. **B9**, 73 (1930).

[5] C. A. Wert, Phys. Rev. **79**, 601 (1950).

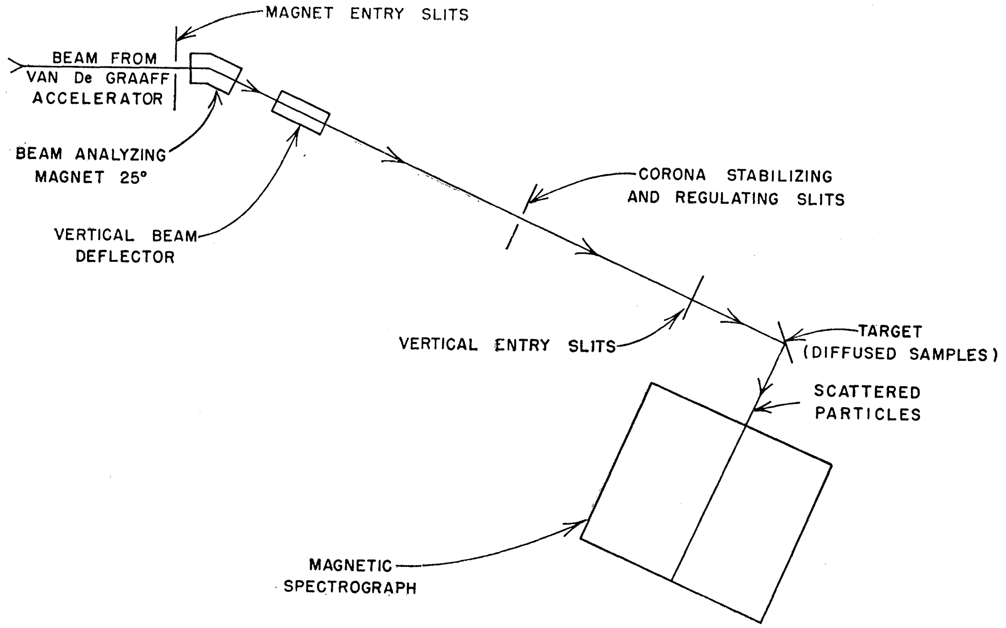

FIG. 1. Schematic layout of spectrograph and associated equipment.

the system (Fe-Ag) at high temperatures.[6] Furthermore, it is in the low-temperature region where one could hope to induce a vacancy density considerably larger than that which obtains at thermal equilibrium. Therefore, it should be possible to study directly the effects of radiation, plastic deformation, etc., on the diffusion process.

This paper describes a method based on elastic particle scattering in which the total depth of investigation is $<10^{-5}$ cm, therefore extending the range to 10^{-18} cm^2/sec. The method used here is a nonsectioning technique, although it is entirely feasible to use the spectrograph for surface concentration determinations in connection with the sectioning method. In either case it is preferable that the diffusing atoms be heavier than the solvent atoms, and in the nonsectioning technique, considerably heavier. It is, however, possible to obtain data of reduced accuracy when the reverse situation obtains if the solubility is appreciable.

An interesting feature of the method demonstrated in this paper is that although the specimens are polycrystalline (mean grain size ≈ 0.01 cm) the ratio of grain size to depth of investigation is so large (≈ 1000) that grain boundary diffusion effects are thus eliminated from the measurements.

DIFFUSION

Specimens and Technique

The copper used was obtained in the form of 7-mm rods, 99.999% pure, from Johnson Mathey and Company. These were milled into $\frac{1}{4}$ in.$\times\frac{1}{2}$ in. blanks, $\frac{1}{16}$ in. thick. The blanks were polished with 0000 metallographic emery paper, then electropolished using a standard phosphoric acid method. The specimens were rinsed in de-ionized, de-aerated water and kept immersed for the few minutes necessary to transfer them to the electroplating bath. The blanks were then plated with ≈ 4 μg/cm^2 of gold in a standard double cyanide solution. The specimens were then sealed in Pyrex ampoules evacuated to 10^{-6} mm Hg.

The diffusion anneals were carried out in a regulated oven in which a massive block of aluminum served for thermal inertia. Thermocouples inserted in the block adjacent to the specimen wells indicated a temperature stability of about ±1°C. These thermocouples were calibrated against a National Bureau of Standards certified platinum-platinum 10% rhodium thermocouple.

Equipment and Experimental Procedure

The magnetic spectrograph has been widely used for measurement of excited state Q values and for precision mass determinations. Rubin has demonstrated the usefulness of a magnetic spectrometer in the chemical analysis of surfaces by particle scattering and has suggested the possibility of determination of continuously varying concentration distributions with minute depth resolution.[7]

The spectrograph used in this investigation is a 40-cm instrument of the broad-range type developed by Buechner.[8] Figure 1 shows a schematic layout of the system used. The diffused specimens as targets were bombarded with protons from a 2-Mev High Voltage

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[6] D. Lazarus and B. Okkerse, Phys. Rev. **105**, 1677 (1957).

[7] Rubin, Passel, and Bailey, Anal. Chem. **29**, 736 (1957).

[8] C. P. Browne and W. W. Buechner, Rev. Sci. Instr. **27**, 899–907 (1956).

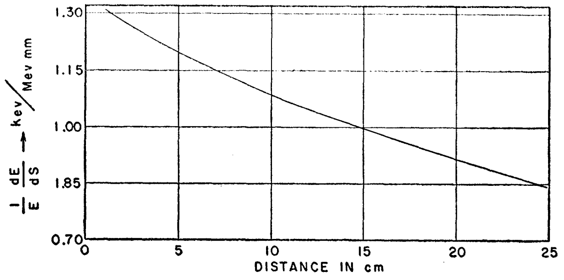

FIG. 2. Measured values of $D\equiv(1/E)(dE/ds)$ *vs* distance s along focal surface.

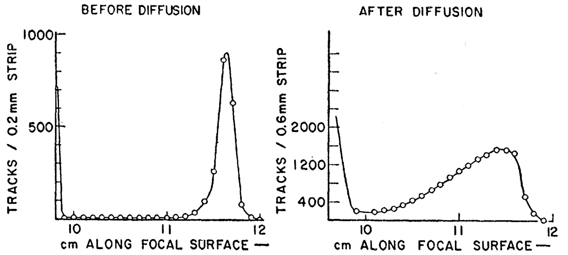

FIG. 3. Proton spectra of gold on copper before and after diffusion at 440°C for 2 hours. $E_p=1.881$ Mev, angle of scattering 90°. Thickness of gold layer $\approx 4\ \mu g/cm^2$.

Engineering Corporation Van de Graaff accelerator. The bombarding energy was standardized at 1.881 Mev using the $Li^7(p,n)Be^7$ threshold. The magnet entry slit was about $\frac{1}{2}$ mm in width. The combination of corona stabilizing and entry slits permitted a region of the target $\frac{1}{2}$ mm×3 mm to be illuminated by the proton beam. All scatterings were carried out at 90°. The scattered protons are dispersed according to energy along the focal surface where they impinge on a 2- ×10-inch NTA nuclear emulsion plate. Eight strips 8 mm wide may be exposed without disrupting the vacuum system. The recorded particle spectrum is determined by microscopic examination of the developed plates. Proper interpretation of the particle spectra permits a determination of the concentration distribution of diffused solute. The energy range of the spectrograph for a given field setting is 1.3 of the median energy. The measured value of solid angle of acceptance is about 5×10^{-4} sterad and varies slightly with position along the focal surface. The measured quantity defined as $D=(1/E)(dE/dS)$, involving the reciprocal of energy dispersion of the spectrograph, is shown in Fig. 2, where S equals distance along the focal surface.

Typical proton spectra of a sample before and after diffusion are shown in Fig. 3. The line shape of the undiffused gold layer is about that obtained for an infinitesimally thin layer. The width ($\approx$4 kev) is due to the sum of all factors leading to an energy spread in the scattered particles, such as beam spread, magnet stability, finite apertures, etc. The rise below 10 cm is in each case due to scattering from the copper solute.

ANALYSIS OF DATA

At 90 degrees, the energetics of scattering is particularly simple. A particle of mass M_1 and energy E_0, elastically scattered by a particle of mass M_0 considered at rest, is reduced in energy to E_s according to the relation

$$\frac{E_s}{E_0}\equiv k^2=\frac{M_0-M_1}{M_0+M_1}. \tag{1}$$

If the scattering element is in a layer which is thin relative to the energy loss of the particles, a narrow group is obtained (i.e., the thin gold group, Fig. 3). However, if the scattering element is distributed in depth, ionization and excitation energy losses spread the spectrum and an extended distribution such as shown in Fig. 3 is obtained.

Now in a thick target containing various elements A_i, with atomic density N_i, distributed uniformly throughout the specimen, the number of particles Y_j scattered by the element A_j and counted in the spectrograph in unit energy interval is

$$Y_j=6.25\times10^{12}N_j\left(\frac{d\sigma}{d\Omega}\right)_j q\Omega\left[\sum_i N_i\left(\epsilon_{i1}k_j^2+\epsilon_{i2}\frac{\cos\theta_1}{\cos\theta_2}\right)\right]^{-1}, \tag{2}$$

where $(d\sigma/d\Omega)_j$= differential scattering cross section/atom steradian in center-of-mass coordinates, q= incident charge in microcoulombs, Ω= spectrograph solid angle in sterad (center-of-mass system), θ_1= angle between incident beam and a normal to the target, θ_2= angle between scattered beam and a normal to the target, ϵ_{i1}= stopping cross section before scattering, ϵ_{i2}= stopping cross section after scattering. Y_j is an implicit function of energy through the dependence of the ϵ's and $d\sigma/d\Omega$ on energy. However, for the energy intervals involved in this paper the ϵ's and $d\sigma/d\Omega$ are constants within 1%. Therefore, Y_j is proportional to N_j. Now, if N_j is not constant but varies with depth then Y_j will be a corresponding function of energy, where the relation between energy and depth of penetration into the sample is given by

$$(E_s-E)=\sum_i N_i\left(\frac{\epsilon_{i1}}{\cos\theta_1}k_j^2+\frac{\epsilon_{i2}}{\cos\theta_2}\right)x, \tag{3}$$

where E_s is the energy of protons scattered from the surface, and x is depth into the target surface. In practice, for very thin solute layers, one can ignore solute, applying Eq. (3) only to solvent species, without incurring significant error.

Energy is readily convertible to distance along the plate by

$$E_s-E=DE\Delta S, \tag{4}$$

where the differential form is accurate to better than

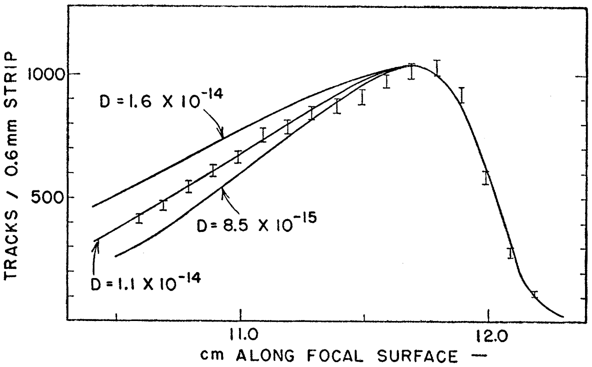

FIG. 4. Convolution of spectrograph resolution function with solutions of the diffusion equation for several assumed diffusion coefficients, compared with the elastic proton spectrum obtained from a sample annealed at 503°C for 1 hour. $E_p = 1.881$ Mev, depth resolution $dx/ds = 9.042\times10^{-7}$ cm/mm, where s = distance along focal surface.

1% over the energy intervals involved here. We find in effect, that the spectrum as recorded, under a simple change of independent variable yields the concentration distribution directly. In practice, of course, Y_j is not directly observed. One rather observes the convolution:

$$Y_{0j}(E)=\int_{-\infty}^{+\infty} g(\eta)Y_j(E-\eta)d\eta, \tag{5}$$

where Y_{0j} is the observed spectrum, and $g(\eta)$ is the spectrometer resolution function normalized to unit area. The function $g(\eta)$ may be determined by bombardment of an ultra-thin target. Since the width of $g(\eta)$ is appreciable compared to the diffused spectra, it is necessary to take account of the convolution in the analysis. The procedure used was to convolve the appropriate solution of the concentration-independent diffusion equation,

$$C(xt)=\frac{S}{(\pi Dt)^{\frac{1}{2}}}\exp\left(-\frac{x^2}{4Dt}\right), \tag{6}$$

with the spectrometer resolution function for several assumed D values, and to compare the results with the data. For convenience, the convolutions were carried out in units of distance along the focal surface.

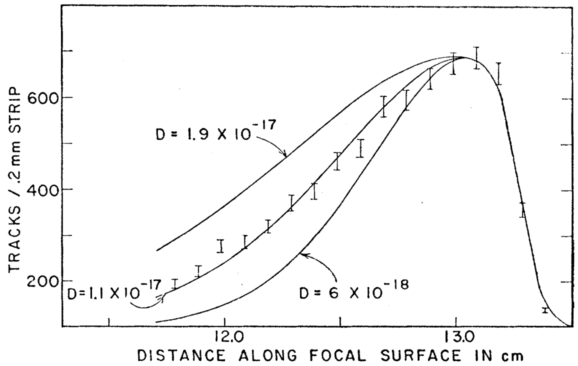

FIG. 5. Elastic proton spectrum obtained from a sample annealed at 352°C for 495.75 hours, compared with the convolved solutions of the diffusion equation for several assumed D values $E_p = 1.881$ Mev, $dx/ds = 9.042\times10^{-7}$ cm/mm.

A complication arises at the lower temperatures for the Au-Cu system where α' and α'' phases are possible. In this region, the thin-layer boundary condition is not strictly applicable in the early stages of diffusion. However, a resort to the numbers involved shows that all solubility constraints are removed during diffusion in a surface layer which is thin compared to the depth resolution of the spectrograph. It therefore appears that the procedure used does not introduce an appreciable error.

RESULTS

The experimental results are summarized in Table I. Comparison of the proton spectra with the convoluted solutions of the diffusion equation are shown in Figs. 4 and 5 for the highest and lowest temperatures. The fits obtained define the diffusion coefficients within about 10%. The mean penetration of solute was rather small for the points at 362 and 389 degrees. In order to improve the depth resolution, these two samples were analyzed using 1.88-Mev deuterons. One of these spectra is illustrated in Fig. 6. In this case, the depth resolution is 6.55×10^{-7} cm per mm distance along the focal surface. This illustrates the point, which may be readily verified by recourse to the expressions given under analysis of data, that to improve depth resolution one may either decrease the bombarding energy or increase the mass of the scattered particle. By pushing this point to the practical limit, it should be possible to directly measure diffusion coefficients as low as 10^{-20} cm²/sec without inconveniently long annealing times.

A plot of ln$D$ *vs* $1/T$ is shown in Fig. 7. The best straight line fit to these data is extrapolated upward and compared with the recent precise measurements of Tomizuka[9] in the temperature range 700°–1030°. The individual data points fit the straight line with a root mean square deviation of 12.6%. The equation of this line is

$$D=(0.104\pm0.06)\exp(45\,750\pm750/RT)\quad \text{cm}^2/\text{sec}.$$

Absolute accuracy of the points is believed to be better

TABLE I. Experimental results for gold-copper diffusion.

T (°C)	Duration of anneal (hours)	D (cm²/sec)
503	1	1.2×10^{-14}
457	2	1.8×10^{-15}
457	2	2.2×10^{-15}
432	6.25	7.0×10^{-16}
389	20	9.0×10^{-17}
362	96	1.5×10^{-17}
352	495.75	1.1×10^{-17}

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[9] C. T. Tomizuka (private communication).

than ±20%. The principle source of error as regards absolute accuracy is in the measured value of stopping cross section. The values used in the calculations were obtained from the compilation of Fuchs and Whaling.[10] However, a separate experiment was performed to check the stopping cross sections used. The results agreed with Fuchs and Whaling within 5%.

Annealing times shorter than one hour were not attempted in the oven setup. However, it should be possible to close the gap between the present method and the sectioning range, by developing techniques for accurate heating of specimens for short times of the order of seconds.

DISCUSSION

As may be seen from Fig. 7, the agreement between the present results and the data of Tomizuka is quite good, and establishes that the Arrhenius law is valid to first approximation over a variation of eight orders of magnitude. The apparent decrease in slope with decreasing temperature is probably due to diffusion along internal surfaces. Tomizuka's result in his range (dotted line Fig. 7) is $D=(0.69\pm 0.07)\exp(49\,700 \pm 500/RT)$. The present investigation therefore shows a decrease in activation energy of 3950 cal/mole over 678°C. It is very interesting that this result of 5.8 cal/mole°C agrees so closely with the 6 cal/mole°C found by Tomizuka[11] in his re-examination of the data on the diffusion of antimony in silver. In the present case, the condition of Hart[12] that a diffusing atom encounter many dislocations in distances of the order of the depth of investigation is probably not valid. Therefore, we might expect deviations from the Gaussian distribution given in (6). The distributions observed are certainly Gaussian to first order (see Figs. 4, 5, and 6); however, there was a persistant tendency for the low-concentration data to fall outside statistics toward greater penetration. The cause of these small but persistent deviations is not yet understood.

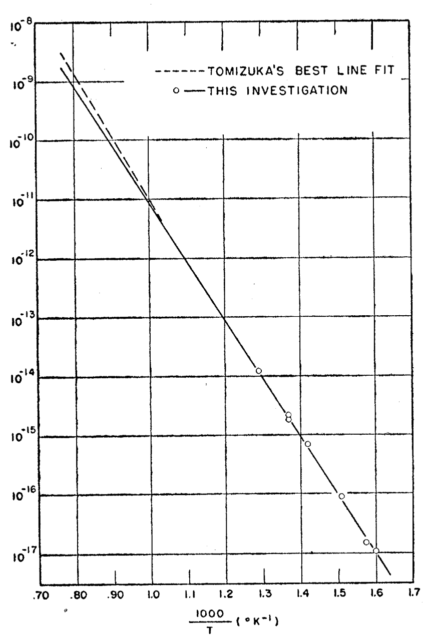

FIG. 7. Plot of $\ln D$ vs $1/T$. The solid line is the best straight-line fit of the data of this investigation, extrapolated upward into the sectioning range. The dashed line is the result of C. T. Tomizuka for the range indicated.

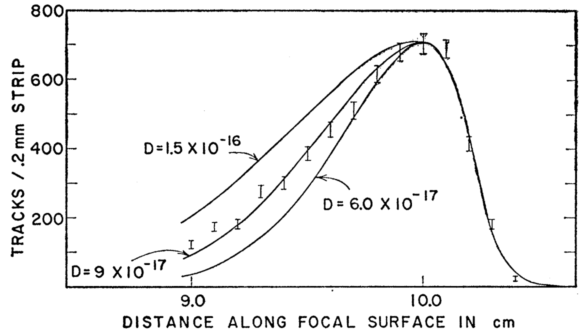

FIG. 6. Elastic deuteron spectrum obtained from a sample annealed at 375°C for 20 hours, compared with the convolved solutions of the diffusion equation for several assumed D values $E_d=1.88$ Mev, $dx/ds=6.546\times10^{-7}$ cm/mm.

ACKNOWLEDGMENTS

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[10] R. Fuchs and W. Whaling, California Institute of Technology (unpublished).

[11] C. T. Tomizuka, Acta Met. 6, 660 (1958).

[12] E. W. Hart, Acta Met. 5, 597 (1957).