

Effect of High Pressure on Self-Diffusion in Concentrated FeCo Alloys*

S. G. Fishman

Naval Weapons Laboratory, Dahlgren, Virginia 22448

and

R. N. Jeffery†

Department of Physics and Materials Research Laboratory,
University of Illinois, Urbana, Illinois 61801

(Received 14 January 1971)

The effect of high pressure on the diffusion of Fe^{59} in near-equiatomic FeCo alloys has been measured at 944.5°C. The value of the activation volume determined from these measurements is $4.38 \pm 0.89 \text{ cm}^3/\text{mole}$ or 0.60 ± 0.12 times the molar volume. ΔK obtained from this value of ΔV is compared to the earlier reported value from isotope-effect measurements, $\Delta K = 0.73$. The values of both of these parameters indicate that diffusion in the disordered phase of bcc FeCo is similar to that expected for a simple monatomic metal.

In recent work, measurements of the mass dependence or isotope effect for self-diffusion in near-equiatomic FeCo alloys have been reported.¹ It was found that in the fcc and disordered bcc phases of this system, the magnitude of the isotope-effect parameter $E_{F_e} = f_{F_e} \Delta K$ was approximately equal to values found in corresponding monatomic metals, where diffusion is by a simple monovacancy mechanism. In the ordered bcc region, however, E_{F_e} was observed to decrease drastically with decreasing temperature, which could indicate an increasing amount of correlation. This effect is consistent with the high degree of correlation expected for the six-jump vacancy mechanism thought to be operative in such CsCl-type ordered metallic alloys.^{2,3} In the expression for E , f is the correlation factor and ΔK is defined as the fraction of the total kinetic energy of a single diffusion jump which is possessed by the jumping atom. By its definition, ΔK is thus closely related to the degree of nontracer atom participation in the diffusion jump process.

Another parameter which measures the cooperative motion of nontracer atoms, or the amount of relaxation around lattice defects, is the activation volume ΔV determined from measurements of the pressure dependence of diffusion.⁴ In this note are reported measurements which were made of the diffusion at several pressures of Fe^{59} in the disordered bcc phase of near-equiatomic FeCo alloys. The value of the activation volume so obtained is compared with those measured in other metallic systems and with the approximate value of ΔK calculated previously for this alloy system.

The growth and preparation of the large-grained FeCo specimens used in this work were the same as described previously.¹ The specimens were hand polished and plated with Fe^{59} by evaporation. A thin polished cap of FeCo was then pressure

welded to the plated face using a molybdenum welding rig similar to that described by Mock.⁵ The purpose of the cap was to prevent oxidation or evaporation of the tracer during the diffusion anneal.

The high-pressure diffusion anneals were carried

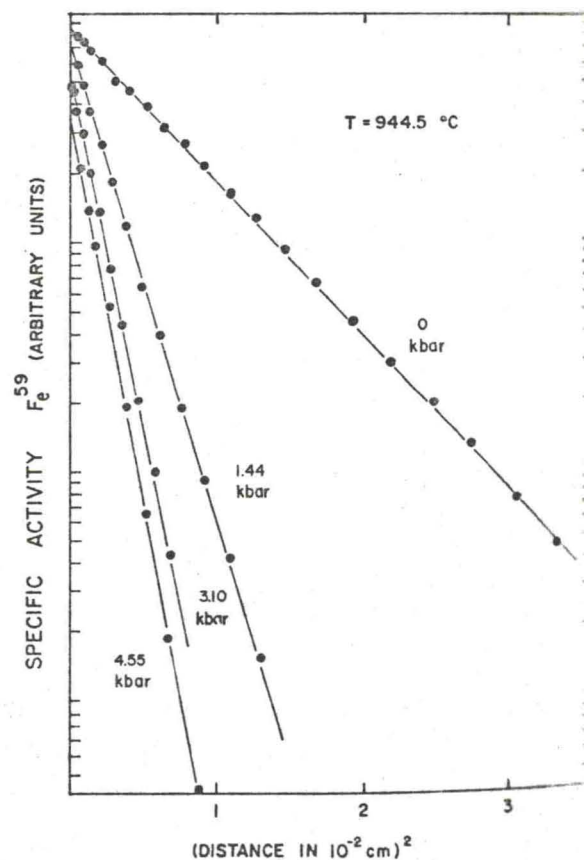


FIG. 1. Penetration profiles for diffusion of Fe^{59} into equiatomic FeCo alloys at 944.5°C.

TABLE I. Variation of diffusivity of Fe⁵⁹ with hydrostatic pressure at 944.5 °C.

Pressure (kbar)	<i>D</i> , (cm ² /sec)
0	(5.52 ± 0.15) × 10 ⁻¹¹
1.44 ± 0.01	(5.33 ± 0.06) × 10 ⁻¹¹
3.10 ± 0.01	(4.94 ± 0.09) × 10 ⁻¹¹
4.55 ± 0.03	(4.53 ± 0.07) × 10 ⁻¹¹

out in an argon atmosphere using an internally heated high-pressure vessel.⁶ The thermocouple was cemented inside a FeCo dummy piece in order to correctly measure the temperature of the sample. The temperature was controlled automatically and was constant to approximately ± 0.5 °C. A pressure correction of 0.5 °C/kbar was assumed for the Pt-Pt-10 at. % Rh thermocouple.⁶ The pressure was maintained constant usually to 1% or better over the duration of the 24-h runs. The zero-pressure anneal was carried out in a vacuum furnace using a welded specimen identical to the pressure specimens.

The samples were analyzed by the standard techniques of lathe-sectioning and counting, with appropriate corrections made for welding and warm-up time, equipment drifts, tracer decay, and background activity. The sections were contained in thin cellulose acetate butyrate vials and counted with an NaI (Tl) well-type scintillation detector.

The penetration profiles [plots of log (specific activity) versus penetration distance squared] for diffusion of Fe⁵⁹ in equiatomic FeCo alloys at 944.5 °C and 0, 1.44, 3.10, and 4.55 kbar are shown in Fig. 1. The diffusion coefficients are given in Table I and shown graphically in Fig. 2. The largest single source of error in the *D* values is uncertainty in the temperature measurements. (A 2 °C error in temperature results in about a 4% error in *D*.) Other sources of error, such as weighing, counting, anneal time, etc., were of the order of 1% or less combined, so that we estimate the uncertainties in *D* values to be approximately 3-4%.

The activation volume is calculated according to^{4,7}

$$V = -RT \frac{\partial \ln D}{\partial P} + RT \gamma_G K_T, \quad (1)$$

where γ_G is the Grüneisen constant, K_T is the isothermal volume compressibility, and the other terms have their usual meanings. The second term of Eq. (1) is small compared to the first, and will be discussed below. From the first term of Eq. (1), the activation volume is computed to be 4.34 cm³/mole, from a least-squares determination of the slope of Fig. 2. The standard deviation in the

slope, considering just the data points themselves, is $\sigma(\Delta V) = 0.35$ cm³/mole. However, allowing for a reasonable temperature uncertainty of ± 1.5 °C, the corresponding uncertainty in *D* leads to a variance in the slope of $\sigma(\Delta V) = 0.89$ cm³/mole. It is considered that the small variance in the first instance is probably fortuitous, and that the latter figure more realistically characterizes the experimental data.

The second term of Eq. (1) is estimated to be approximately 0.04 cm³/mole, based on the Grüneisen relation $\gamma_G K_T = 3\alpha V/C_v$,⁸ and available values or estimations of the thermal expansion,⁹ specific heat,¹⁰ and compressibility.¹¹ The molar volume (at room temperature) is determined to be 7.09 cm³/mole, based on the measured density of these alloys (8.10 g/cm³) and the average atomic weight of Fe and Co. The molar volume at 944.5 °C is then approximately 7.33 cm³/mole. The final value of the activation volume is thus

$$\begin{aligned} \Delta V &= 4.38 \pm 0.89 \text{ cm}^3/\text{mole} \\ &= 0.60 \pm 0.12 V_M, \end{aligned} \quad (2)$$

where V_M is the molar volume.

The value of $\Delta V/V_M = 0.60$ determined in this work may be compared with corresponding values found in other bcc metal systems: 0.52 in Na,¹² 0.28 in Li,¹³ and 0.45-0.60 in the α phase of the Fe-V system.¹⁴ In the latter work, the activation volume for chemical interdiffusion was observed

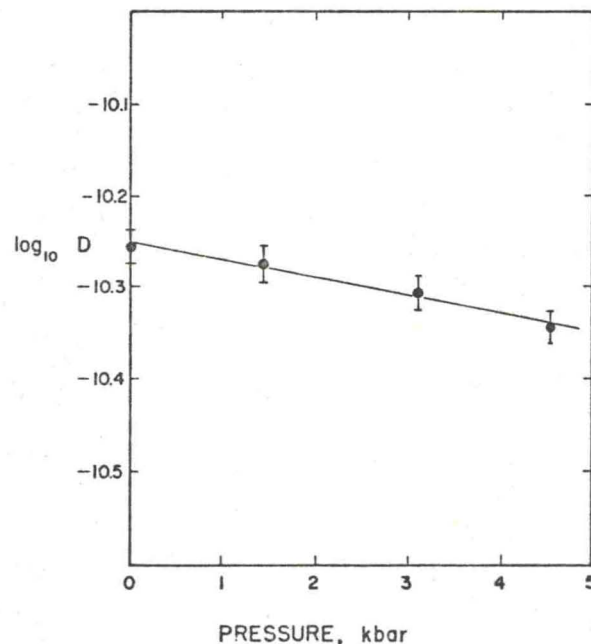


FIG. 2. Diffusion coefficient vs pressure for diffusion of Fe⁵⁹ into equiatomic FeCo alloys at 944.5 °C.

to decrease with increasing V concentration, very likely due to the large atomic size difference between Fe and V atoms, allowing for greater openness at large V concentration. In FeCo, however, where the atoms are very nearly the same size, the activation volume for self-diffusion in the disordered bcc phase is equal to approximately what one would expect for a monatomic metal. Measurements in the fcc alloy Au-34 at. % Ag, where the atoms are also the same size, show a similar effect.¹⁵

Gupta and Jeffery have made measurements of the effect of pressure on diffusion in ordered AuZn alloys of near-equiatomic composition.¹⁶ In that system the activation volume for 50:50 composition was found to be approximately 1.1 times the molar volume, indicating that outward relaxation of the atoms around a vacancy actually takes place. The reason for this large activation volume is thought to be closely related to the nature of the ordering energy in these CsCl-type alloys. Other measurements of outward relaxation have been reported in alkali halides¹⁷ and certain close-packed polyvalent metals (Al and Be).^{18,19} The former shows the strong influence of Coulombic repulsion of next nearest neighbors around vacancies in an ionic crystal and the latter presumably reflects oscillations in the screening potential surrounding vacancies in metals. The low value of $\Delta V/V_M$ for disordered FeCo compared to ordered AuZn illustrates quite dramatically what an important role the ordering energy plays in determining crystal properties.

Measurements of the isotope-effect parameter ΔK for FeCo alloys¹ likewise points up the similarity of disordered FeCo and simple monatomic metals. Several correlations have been suggested between ΔK and ΔV . Barr and Mundy observed that for several metals $\Delta K \sim \Delta V/V_M$, with large values of ΔK going with large values of $\Delta V/V_M$, and vice versa.²⁰ In Zn, however, ΔK is 0.88–0.93,^{21,22} whereas $\Delta V/V_M$ is only 0.44.²³ Hence this relationship is not generally valid.

Another correlation between ΔV and ΔK was

suggested by LeClaire,²⁴ and is expressed by the relation

$$\Delta K \approx \frac{1}{1 + \frac{1}{3}n(1 - \Delta V_f/V_M)}, \quad (3)$$

where n is the approximate number of atoms which relax in the unstable mode of vibration which leads to the jump and ΔV_f is the activation volume of formation. A value of n of approximately 2–3 is deduced from Eq. (3) for FeCo using the estimated value of ΔK (0.73) and $\Delta V_f \approx 0.5V_M$.

Although the exact form of the correlation between ΔK and ΔV is not apparent at the present time, it seems clear that they are closely related in some way. It is to be hoped that future measurements of the two parameters in a larger number of systems may lead to a more complete picture of the defect structure in crystals.

It would clearly be of interest to measure the activation volume in FeCo in the ordered as well as the disordered phase. However, since the magnitude of D in the ordered phase is 10^{-13} cm²/sec or smaller,¹ the anneal times required would be prohibitively long for high-pressure diffusion experiments (of the order of 30 days). An alloy system in which high-pressure measurements in both ordered and disordered phases would be possible is β CuZn. In such a system, the ratio $\Delta V/V_M$ would be expected to become larger as the degree of long-range order increases.

In conclusion, we have found that the activation volume for diffusion of Fe⁵⁹ in near-equiatomic FeCo alloys is equal to 4.38 ± 0.89 cm³/mole or 0.60 ± 0.12 times the molar volume at 944.5°C and over the pressure range 0–5 kbar. This value of ΔV , coupled with the previously reported value of the isotope-effect parameter ΔK , indicates that diffusion in disordered bcc FeCo is quite similar to that expected for a simple monatomic metal.

The authors wish to thank Professor D. Lazarus for his interest in this work and Dr. D. Gupta and Professor D. S. Lieberman for allowing access to their review paper in advance of publication.

*Work supported in part by the U. S. Atomic Energy Commission.

†Present address: Department of Physics and Astronomy, Rensselaer Polytechnic Institute, Troy, N. Y. 12181.

¹S. G. Fishman, D. Gupta, and D. S. Lieberman, Phys. Rev. B **2**, 1451 (1970).

²E. W. Elcock and C. W. McCombie, Phys. Rev. **109**, 605 (1958).

³D. Gupta, D. Lazarus, D. S. Lieberman, Phys. Rev. **153**, 863 (1967); D. Gupta and D. S. Lieberman (unpublished).

⁴D. Lazarus and N. H. Nachtrieb, in *Solids Under*

Pressure, edited by W. Paul and D. M. Warschauer (McGraw-Hill, New York, 1963), p. 43.

⁵W. Mock, Jr., Phys. Rev. **179**, 663 (1969).

⁶R. N. Jeffery, Ph. D. thesis (University of Illinois, Urbana, Ill., 1970) (unpublished).

⁷R. N. Jeffery and D. Lazarus, J. Appl. Phys. **41**, 3186 (1970).

⁸C. Kittel, *Introduction to Solid State Physics*, 3rd ed. (Wiley, New York, 1966), p. 183.

⁹M. E. Fine and W. C. Ellis, Trans. ADME **175**, 742 (1948).

¹⁰H. Asano, Y. Bando, N. Nakanishi, and S. Kachi, Trans. Japan Inst. Metals **8**, 180 (1967).

- ¹¹D. N. Yoon and R. N. Jeffery, *J. Phys. Chem. Solids* (to be published).
- ¹²N. H. Nachtrieb, J. A. Weil, E. Catalano, and A. W. Lawson, *J. Chem. Phys.* **20**, 1189 (1952).
- ¹³R. A. Hultsch and R. G. Barnes, *Phys. Rev.* **125**, 1832 (1962).
- ¹⁴R. E. Hanneman, R. E. Ogilvie, and H. C. Gatos, *Trans. Met. Soc. AIME* **233**, 691 (1965).
- ¹⁵E. D. Albrecht and C. T. Tomizuka, *J. Appl. Phys.* **35**, 3560 (1964).
- ¹⁶D. Gupta and R. N. Jeffery (unpublished).
- ¹⁷D. N. Yoon and D. Lazarus, *Bull. Am. Phys. Soc.* **15**, 381 (1970); D. Lazarus, D. N. Yoon, and R. N. Jeffery, *Europhysics Conference on Atomic Transport in Solids and Liquids*, Marstrand, Sweden, 1970 (unpublished).

- ¹⁸M. Beyeler and Y. Adda, *J. Phys. (Paris)* **29**, 345 (1968); B. M. Butcher, H. Hutto, and A. L. Ruoff, *Appl. Phys. Letters* **7**, 34 (1965).
- ¹⁹M. Beyeler and D. Lazarus, *Europhysics Conference on Atomic Transport in Solids and Liquids*, Marstrand, Sweden, 1970 (unpublished).
- ²⁰L. W. Barr and J. N. Mundy, *Diffusion in Body-Centered Cubic Metals* (American Society for Metals, Metals Parks, Ohio, 1965), p. 171; J. N. Mundy, L. W. Barr, and F. A. Smith, *Phil. Mag.* **14**, 785 (1966).
- ²¹A. P. Batra, *Phys. Rev.* **159**, 487 (1967).
- ²²N. L. Peterson and S. J. Rothman, *Phys. Rev.* **163**, 645 (1967).
- ²³L. Chabildas and H. M. Gilder (unpublished).
- ²⁴A. D. LeClaire, *Phil. Mag.* **14**, 1271 (1966).

PHYSICAL REVIEW B

VOLUME 3, NUMBER 12

15 JUNE 1971

ERRATA

F-Center Gap Mode in Alkali Halides. A Molecular Model, R. S. Singh and S. S. Mitra [*Phys. Rev. B* **2**, 1070 (1970)]. Dr. D. Bäuerle has brought to our attention certain misinterpretations of his results. The sentences starting from line 3 and ending in line 16 of the second paragraph of p. 1072 should accordingly be changed to "... For the *F* center in KI, a sharp band at 83 cm⁻¹ has been observed¹ in the far-infrared absorption. Clearly this should be compared with the calculated frequency of 81.2 cm⁻¹ (*F*'_{1u}). More recently Bäuerle and Hübner [*Phys. Rev. B* **2**, 4252 (1970)] have reported the observation of a gap mode due to an *F* center in KBr at 99.6 cm⁻¹ (1.2 °K). This compares well with our calculated value of 92.6 cm⁻¹ (300 °K) for this center. A resonant-band mode peaking around 62 cm⁻¹ has been reported^{6,14} for the KI:H⁻ system."

Nonresonant Interband Faraday Rotation in Silicon, Cedric J. Gabriel [*Phys. Rev. B* **2**, 1812 (1970)]. A printer's error was made in Eq. (3). The correct form of the equation is

$$2\gamma = [\xi(-) - \xi(+)] \left(\frac{d\xi(\pm)}{d\alpha} \right)^{-1}$$

High-Temperature Measurements of the Electron Hall Mobility in the Alkali Halides, C. H. Seager and David Emin [*Phys. Rev. B* **2**, 3421 (1970)]. To correct for an error which has been discovered in the calibration procedure of the apparatus, the quoted Hall mobilities for all samples measured should be multiplied by a factor of 1.24 to obtain the proper values. This correction in no way affects the conclusion drawn by the authors that con-

tinuum polaron theories are inadequate in their predictions of the temperature dependence of the data.

Lattice-Dynamical Theory of the Diffusion Process. I. Isotope Effect in Cubic Metals, B. N. Narahari Achar [*Phys. Rev. B* **2**, 3848 (1970)]. The 3*N* normal modes of the lattice perturbed by an isotopic impurity should be labeled by a single index *f*, rather than the symbols (\vec{q}, λ). Accordingly, the symbols (\vec{q}, λ) should be replaced by *f* in the following: (i) Line above Eq. (10), p. 3850. (ii) Equations (10) and (11), p. 3850. (iii) Line 3 from top of the right-hand column, p. 3850.

Ionic Raman Effect. I. Scattering by Localized Vibration Modes, A. A. Maradudin and R. F. Wallis [*Phys. Rev. B* **2**, 4294 (1970)]. An unfortunate numerical error occurred in plotting Figs. 1 and 2 on the basis of Eqs. (17) and (29), respectively. The scattering efficiencies shown in these figures are consequently too large by factors of 10³-10⁴. The corrected results, together with a demonstration that the ionic Raman effect for the system CaF₂:H⁻ dominates the electronic Raman effect when the incident light is in the infrared, are presented in a paper by L. B. Humphreys, A. A. Maradudin, and R. F. Wallis to appear in *Physics of Impurity Centres in Crystals* (Academy of Sciences of the Estonian S.S.R., Tartu, 1971).

Electromodulation of the Optical Properties of Thallium-Activated Potassium Bromide, U. Giorgianni, V. Grasso, and G. Saitta [*Phys. Rev. B* **2**, 5007 (1970)]. Figures 1 and 2 should be interchanged,