

Pressure Dependence and Isotope Effect of Self-Diffusion in a Metallic Glass

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The pressure dependence and isotope effect of cobalt diffusion have been measured in amorphous $\text{Co}_{76.7}\text{Fe}_2\text{Nb}_{14.3}\text{B}_7$ and in fcc Co. Within experimental accuracy no pressure dependence and an isotope effect $E = (D_\alpha/D_\beta - 1)/[(m_\beta/m_\alpha)^{1/2} - 1] = 0.1$ were found in $\text{Co}_{76.7}\text{Fe}_2\text{Nb}_{14.3}\text{B}_7$. These results show that diffusion in the metallic glass is not mediated through quasivacancies in thermal equilibrium similar to crystalline Co. Diffusion rather occurs via a direct mechanism involving about ten atomic masses.

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During the last decades diffusion in amorphous alloys has been studied extensively.¹⁻⁶ Nevertheless, the level of understanding of the underlying mechanisms is still rather limited and basic questions are controversial. Many investigators did not properly take into account relaxation phenomena, which can lead to time-dependent diffusivities and a drop of the diffusion coefficient of more than 1 order of magnitude.^{7,8} Horváth *et al.*⁷ have shown that the drop of the diffusivity due to relaxation and diffusion in the relaxed amorphous state are often controlled by different activation energies. The first one is attributed to the annihilation of excess free volume and is, hence, not related to diffusion in the metastable amorphous state, which is characterized by a diffusivity independent of time.^{7,8}

As in crystals an Arrhenius type of behavior with constant activation energy Q and a preexponential factor D_0 , indicative of a thermally activated process, is generally observed for diffusion in metallic glasses within the relatively small temperature range experimentally accessible. Diffusion can be enhanced by irradiation, which in crystalline materials produces additional point defects.⁹ Measurements of the pressure dependence of crystallization have yielded an activation volume of the order of one atomic volume.¹⁰ These and other experiments, though they do by no means provide direct evidence, have led to the conclusion that diffusion is mediated by point defectlike entities, which also may be in thermal equilibrium.^{6,9-13}

On the other hand, some values of D_0 and Q reported in the literature deviate from those usually regarded as an indication of diffusion via thermal quasivacancies by many orders of magnitude. Particularly for Zr diffusion in $\text{Fe}_{24}\text{Zr}_{76}$ with extremely large values for D_0 and Q , Frank, Horváth, and Kronmüller⁸ have proposed a collective mechanism.

In order to elucidate the basic diffusion mechanisms, not much additional information is to be expected from further measurements of diffusivities. Knowledge rather is needed of the activation volume and the isotope effect of diffusion. Corresponding experiments have not yet been carried out due to the experimental difficulties involved.

In this Letter measurements are reported of the pressure dependence of Co diffusion in amorphous $\text{Co}_{76.7}\text{Fe}_2\text{Nb}_{14.3}\text{B}_7$ which directly yield the activation volume and clearly allow us to exclude thermal quasivacancies as carriers of diffusion. In addition, data on the isotope effect are presented. From these data the number of atomic masses participating in the diffusion process is estimated and implications for the underlying mechanism are discussed.

The experiments were carried out with fully relaxed samples. A radio-tracer technique in combination with ion-beam sputtering (IBS) for serial sectioning was employed.¹⁴⁻¹⁶ To demonstrate that this approach provides the high accuracy required for the present investigations measurements were also performed for crystalline Co.

Melt spun amorphous $\text{Co}_{76.2}\text{Fe}_2\text{Nb}_{14.3}\text{B}_7$ ribbon was kindly provided by Vacuumschmelze Hanau, Federal Republic of Germany. Measurements of the coercive field and electron microprobe analysis showed the sample to be completely amorphous and homogeneous in composition, respectively. A crystallization temperature T_c of 743 K was determined by differential scanning calorimetry (at 10 K/min). Well beyond T_c the specimens were annealed for 6 h at 689 K for relaxation in order to reach the plateau region of the diffusivity. Prior to evaporation of the tracer 90 nm of the surface were removed by sputter cleaning. Foils of polycrystalline Co of 99.996% purity were annealed at 1623 K for 3 d to obtain a grain size of ≈ 0.4 μm .

Co-60 and Co-57 in carrier-free 0.1-m HCl solution were used as tracers for the isotope-effect measurements. During flash evaporation in high vacuum CoCl was thermally decomposed and ≈ 40 kBq of Co-60 and Co-57, each, corresponding to about one monolayer, were deposited on the sample simultaneously. Annealing at high pressure was carried out in a special setup under hydrostatic conditions in Ar atmosphere. X-ray diffraction was employed to check that the samples were still completely amorphous after heat treatment. Serial sectioning was performed by dc ion-beam sputtering with an intense beam of 600-eV argon ions.¹⁶ The material sputtered off was collected on a foil, which was advanced like a film in a camera after each section by a stepping

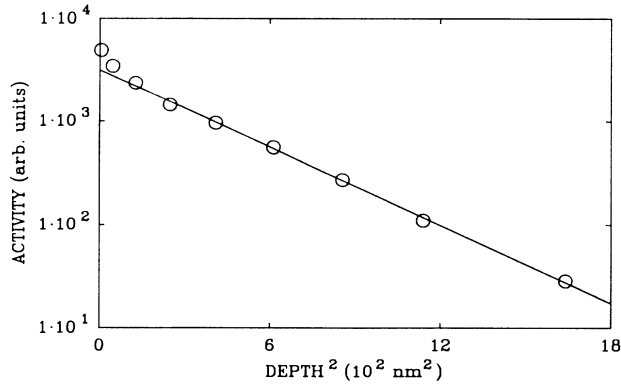


FIG. 1. Penetration profile for Co-57 diffusion into amorphous $\text{Co}_{76.7}\text{Fe}_2\text{Nb}_{14.3}\text{B}_7$ at $T=642$ K. The Co-57 activity is plotted vs the square of the penetration depth.

motor without interrupting the sputter process. The ion current was kept constant electronically within $\pm 0.5\%$. The sputter depth was calculated from the total depth, measured gravimetrically, and the sputter time. The γ activity of each section was either counted by means of a NaJ well-type scintillation counter or, as for the isotope-effect measurements, by a high-resolution intrinsic Ge detector. The 122- and 136-keV lines were used for Co-57 and the 1.173- and 1.332-MeV lines for Co-60.

A typical penetration profile is shown in Fig. 1. The data were corrected for background activity in the sputter chamber. This contamination, which is usually neglected, is also obtained in a clean chamber due to small fractions of activity from the first highly active sections spread in the chamber.¹⁶ In order to meet the high-precision requirements for the detection of an isotope effect, the correction was indispensable. According to the thin-film solution of Fick's second law¹⁷ the diffusion coefficient D can be extracted from the slope $-1/4Dt$ of the straight line in Fig. 1 and the annealing time t .

The temperature dependence of Co diffusion in amorphous Co-Fe-Nb-B is depicted in Fig. 2. A linear relationship between $\ln D$ and $1/T$ is observed, which yields an activation energy of 2.3 ± 0.2 eV and a preexponential factor of $D_0 = 1 \times 10^{-3} \text{ m}^2/\text{s}$. These values are not much different from those in crystalline solids.¹⁷ Since the analysis of Frank, Horváth, and Kronmüller applies for extreme values for D_0 and Q only, they are not indicative of a particular diffusion mechanism.

In Fig. 3 the Co diffusivity is shown as a function of pressure for the metallic glass and crystalline Co. Within an accuracy of a few percent, the slope directly yields the activation volume of diffusion¹⁸

$$V = -kT \left(\frac{\partial \ln D}{\partial p} \right)_T \quad (1)$$

For fcc Co, $V = (0.71 \pm 0.2) \Omega$ at $T = 1100$ K. Ω is the

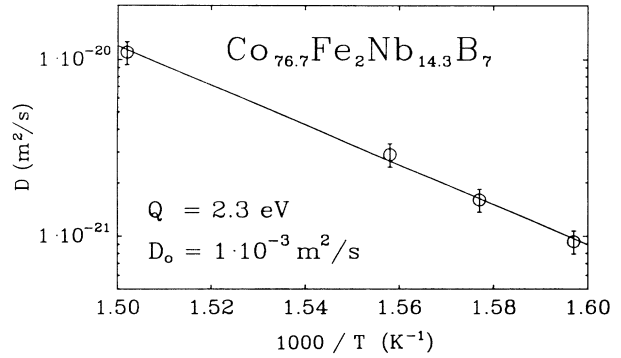


FIG. 2. Arrhenius plot of cobalt tracer diffusion in amorphous Co-Fe-Nb-B. The diffusivity D is depicted as a function of the inverse temperature T on a semilogarithmic scale.

atomic volume of Co. This value is typical of fcc metals where a vacancy mechanism for self-diffusion is well established. Here V essentially represents the volume of a relaxed monovacancy.^{17,19,20} At the low temperature of 1100 K divacancies are negligible. V also contains the migration volume of the vacancy which is regarded as a small contribution of the order of 10%.

No pressure dependence is observed within experimental error margins for amorphous Co-Fe-Nb-B. Figure 3 yields $V = (-0.06 \pm 0.1) \Omega$. This result clearly allows us to exclude quasivacancies in thermal equilibrium as car-

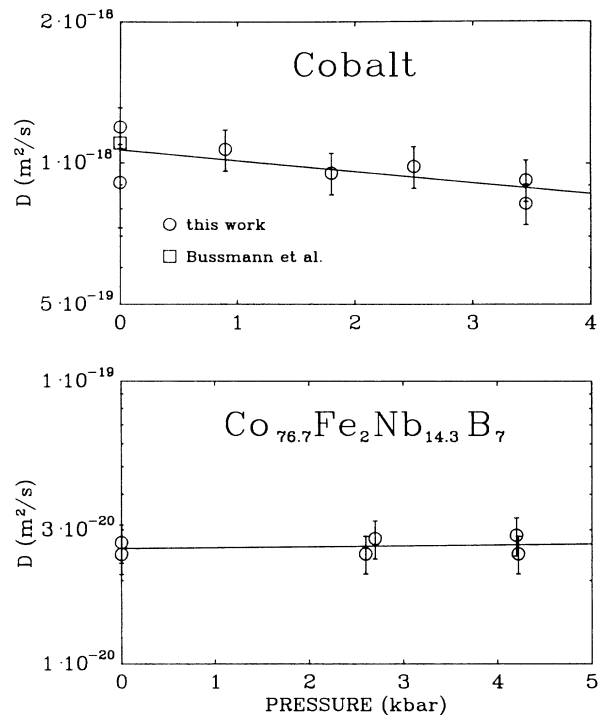


FIG. 3. Diffusion coefficient of Co-60 vs hydrostatic pressure for fcc Co and amorphous Co-Fe-Nb-B at $T = 1100$ and 669 K, respectively.

riers of diffusion in the relaxed amorphous state. It should be pointed out that by comparing the slopes in Fig. 3 one even underestimates the effect in V due to the factor of kT in Eq. (1).

The isotope effect in Co and the amorphous alloy follows from Fig. 4 where $\ln(c_a/c_\beta)$ is plotted versus $\ln c_\beta$. The slope directly yields $D_a/D_\beta - 1$. This expression can be written as^{21,22}

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

Here m_i are the tracer masses, m is the average mass of the matrix, n is the number of jumping atoms, and f is the correlation factor. ΔK accounts for many-body effects. It is the fraction of kinetic energy associated with motion parallel to the jump direction in the saddle-point configuration which resides in the n jumping atoms. For self-diffusion via monovacancies $n=1$ and the correlation factor solely depends on the lattice geometry. For the fcc type, $f=0.782$.¹⁷ From Fig. 4 one obtains $E \equiv (D_a/D_\beta - 1)/[(m_\beta/m_a)^{1/2} - 1] = 0.74 \pm 0.05$ and $\Delta K = 0.95$. This value of ΔK reflects that the jumping tracer is slightly affected only by neighboring atoms. ΔK is always found to be close to unity for a monovacancy mechanism in close-packed structures.¹⁷ The isotope effect measured in this paper is in good agreement with

the temperature dependence of E in Co reported at higher temperatures.²³

For amorphous Co-Fe-Nb-B, Fig. 4 yields $E = 0.10 \pm 0.01$. This small isotope effect corroborates the results for the activation volume. It is not consistent with an indirect diffusion mechanism similar to crystalline solids. For self-diffusion via thermal or nonthermal defects ΔK and f , both, are much too large in relatively close-packed structures to result in $E = 0.1$. Rather a direct mechanism has to be considered. Such a mechanism is not correlated. For $f=1$ the ratio of the diffusivities directly yields the corresponding jump frequency ratios. Hence, Eq. (2) follows directly without the restrictions usually involved for $f \neq 1$.²²

Whether the weak isotope effect is essentially due to a large n in Eq. (2) or a small ΔK cannot be concluded definitely from the measurements. Both descriptions are complementary to a certain extent. One obtains the lower limit of $n \approx 10$ for the number of atoms participating in the diffusion process by attributing the whole effect to n . For the simultaneous motion of ten atoms, all contributing equally, considerably higher values for the activation energy and the preexponential factor than those observed (Fig. 2) are to be expected. n is very much a weighted-average quantity involving some ten atoms.

One arrives at about the same conclusion by considering a single jump mechanism where $n=1$ and $\Delta K \ll 1$. Within this framework, a jump of the tracer is initiated by fluctuations of the free volume, and a hole (large enough for the tracer to jump in) is created by strong displacements of the surrounding atoms opposite to the jump direction. After the jump the structure is completely relaxed. Le Claire²² has established a very rough connection between ΔK , the relaxed unoccupied volume ΔV remaining after the jump, and the number N of atoms which contribute to the relaxation:

$$\Delta K \approx \frac{1}{1 + (N/3)|1 - \Delta V|}. \quad (3)$$

For the present case with $\Delta K = 0.1$ and $\Delta V = 0$, Eq. (3) yields $N \approx 30$ in good agreement with the estimate given above.

In summary, the absence of a measurable pressure dependence of the cobalt diffusivity in $\text{Co}_{76.7}\text{Fe}_2\text{Nb}_{14.3}\text{B}_7$ shows that diffusion is not mediated by thermal quasivacancies. The extremely small isotope effect of $E = 0.1$ further allows us to exclude both thermal and nonthermal defects as carriers of diffusion and gives evidence of a direct mechanism involving some ten atoms. Considering the linear relationship between the preexponential factor and the activation energy, which holds for diffusion of all elements (except H) in all metallic glasses investigated so far,²⁴ one is tempted to suggest an indirect mechanism for diffusion in amorphous alloys in general. Certainly, the number of atomic masses in-

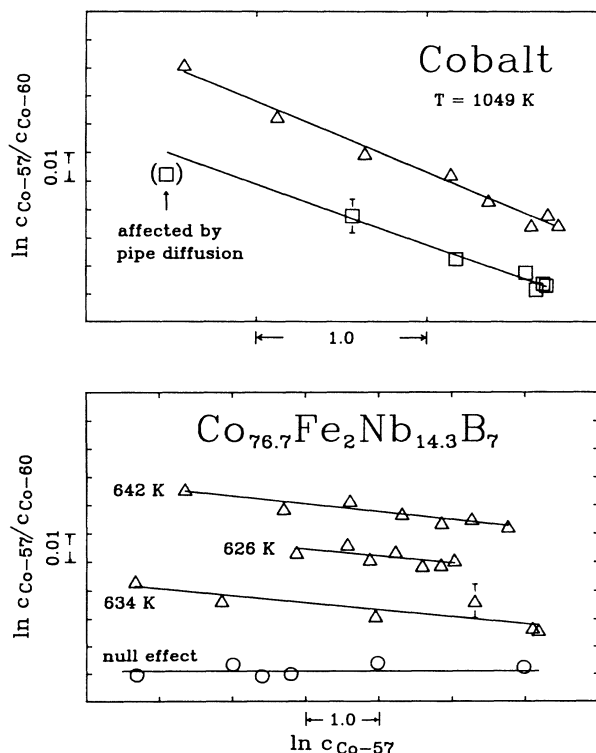


FIG. 4. The activity ratio ($c_{\text{Co-57}}/c_{\text{Co-60}}$) vs $c_{\text{Co-57}}$ on a logarithmic scale for Co diffusion in fcc cobalt and amorphous Co-Fe-Nb-B.

involved will vary from case to case.

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