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The vanishing isotope effect of cobalt diffusion in $\text{Fe}_{39}\text{Ni}_{40}\text{B}_{21}$ glass

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Abstract. The mass dependence of cobalt diffusion has been measured in the structurally relaxed, melt-spun metallic glass $\text{Fe}_{39}\text{Ni}_{40}\text{B}_{21}$ by means of the radio-tracer technique in conjunction with ion-beam sputtering for serial sectioning. Within experimental accuracy no isotope effect $E = (D_\alpha/D_\beta)/((m_\beta/m_\alpha)^{1/2} - 1)$ was observed ($E \leq 0.06$). This result is interpreted in terms of a collective diffusion mechanism involving many atoms.

1. Introduction

Investigations of diffusion in amorphous alloys are important for understanding basic kinetic processes such as structural relaxation and crystallization, as well as the changes in their structure-sensitive properties. In addition, metallic glasses are a paradigm of densely packed disordered structures and therefore of considerable interest for basic research [1]. Apart from the onset of crystallization, which restricts annealing time and temperature for diffusion experiments, metallic glasses undergo the phenomenon of structural relaxation. Here, the diffusivity of as-quenched samples drops, depending on the quenching process, by typically up to one order of magnitude, until it reaches, within experimental accuracy, a time-independent plateau value [2]. Only in this metastable state can experiments of different groups be compared.

One of the main questions of diffusion in metallic glasses is whether it is mediated, as in crystals, by vehicles, i.e. quasivacancies or whether the amorphous structure gives rise to a cooperative rearrangement of several atoms [3, 1, 4, 5]. There are various experimental results that have been interpreted within a quasivacancy model, e.g. the Arrhenius behaviour of the diffusivity or the radiation-enhanced diffusion. On the other hand the large variation of the prefactor over more than 14 orders of magnitude and the activation energy in different alloys and the correlation between them [6, 7] are not expected for a vacancy model. These latter results have promoted the idea of collective diffusion involving several atoms [7]. Highly cooperative diffusion has also been predicted by recent extensions of the mode-coupling theory to the glassy state [8]. Moreover, a direct relationship between collective low-frequency relaxations and diffusion in glasses has been suggested [9, 10].

Measurements of the isotope effect of diffusion are a suitable tool for examining the diffusion mechanism [11]. The definition of the isotope effect reflects a $1/\sqrt{m}$ mass dependence of the attack frequency of the tracer atoms and is usually expressed as

$$E = \left(\frac{D_\alpha}{D_\beta} - 1 \right) / \left(\sqrt{\frac{m_\beta}{m_\alpha}} - 1 \right) \quad (1)$$

with D being the diffusivity of the tracers α and β , respectively. Accordingly, for a single-jump mechanism in densely packed structures E is generally of the order of unity (other than for diffusion of very dilute impurities that interact strongly with defects and thus cause strong correlation effects) [11]. On the other hand, a cooperative mechanism, where the mass effect is diluted by the participation of several atoms, always leads to very small isotope effects [12, 10].

The first isotope-effect measurements in metallic glasses were carried out in $\text{Co}_{76.7}\text{Fe}_2\text{Nb}_{14.3}\text{B}_7$ [12]. We found an extremely low E value of $E = 0.1$ in the well relaxed metal-metalloid glass [12,13]. In addition, the absence of a significant pressure dependence in this glass allowed us to rule out thermally generated defects as diffusion vehicles [14]. These results were interpreted in terms of a cooperative mechanism involving some ten atoms. Recently, measurements in the metal-metal glass $\text{Co}_x\text{Zr}_{1-x}$ ($x = 86, 81$) showed an even lower isotope effect of $E < 0.04$ [10].

In this paper we present measurements of the isotope effect of Co diffusion in amorphous $\text{Fe}_{39}\text{Ni}_{40}\text{B}_{21}$, a well-known and characterized metal-metalloid glass. One measurement was also performed in a $\text{Fe}_{81}\text{Si}_8\text{B}_{11}$ glass. Like in amorphous Co-rich Co-Zr alloys no isotope effect was observed within experimental accuracy. Measurements of the pressure dependence of Co diffusion in the same $\text{Fe}_{39}\text{Ni}_{40}\text{B}_{21}$ glass demonstrating no significant pressure dependence have been reported elsewhere [15].

2. Experimental details

Sample preparation and characterization was the same as in previous investigations [15]. In particular, x-ray measurements showed no sign of crystallinity after all heat treatments (cf figure 1 in [15]). The ribbon was cut into pieces with a diameter of 15 mm by spark erosion. In order to reach the structurally relaxed metastable state, all $\text{Fe}_{39}\text{Ni}_{40}\text{B}_{21}$ samples were preannealed for 420 min at 608 K [2]. In the case of $\text{Fe}_{81}\text{Si}_8\text{B}_{11}$ preannealing was carried out for 120 min at 673 K [16]. Prior to tracer evaporation, the samples were chemically etched. Thereafter, about 180 nm of the surface was removed by ion-beam sputtering. Tracer evaporation was performed in a high-vacuum chamber ($p < 10^{-3}$ Pa), where typically 40 kBq of a mixture of ^{57}Co and ^{60}Co in carrier-free CoCl (Amersham Buchler) were first thermally decomposed and then evaporated from a tungsten boat onto the sample. This corresponds to about one monolayer of Co. The ratio of ^{57}Co to ^{60}Co was chosen to yield nearly equal γ -count rates in the Ge detector [17]. In order to avoid edge contamination, which could lead to severe artifacts in depth profiling, a mask was used to fix the samples onto the heating plate. Under these conditions, the thin film solution of Fick's second law

$$c(x) = \text{constant} \times \exp\left(-\frac{x^2}{4Dt}\right) \quad (2)$$

could be applied in all cases to determine the diffusivity D . Here x is the penetration depth and t the annealing time.

Annealing was performed *in situ* without breaking the vacuum. Temperature was measured and controlled with a Ni-NiCr thermocouple within ± 1 K. Depth profiling was carried out by microsectioning in high vacuum with an intense, electronically controlled beam of 600 eV argon ions [17]. The specimen was mounted on a motor-driven copper holder and the material sputtered off was collected on a foil which was advanced like a film in a camera after each section by a dc motor without interrupting the sputtering process. The sputtering rate (~ 2 nm min^{-1}) was calculated from the total weight loss of the sample

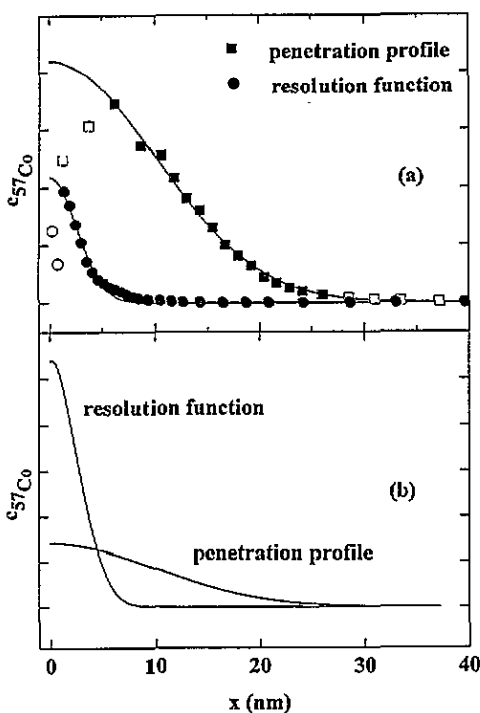


Figure 1. Diffusion profile of ^{57}Co in amorphous $\text{Fe}_{39}\text{Ni}_{40}\text{B}_{21}$ at $T = 623\text{ K}$ and $t = 8.1 \times 10^4\text{ s}$ and resolution function of the present microsectioning technique. The activity, which is proportional to the tracer concentration, is plotted in arbitrary units against the penetration depth x . (a) a fit through the original data (b) normalized to the same activity.

and the sputtering time. After sputtering, the film was cut into pieces corresponding to the individual sections. Special care was taken to ensure a reproducible counting geometry [13]. An intrinsic Ge detector was instrumental in counting the γ -activity of each section. In the measurement of very small isotope effects the influence of a slight detector-specific counting-rate dependence of the activity ratio $I_{\text{Co-57}}/I_{\text{Co-60}}$ has to be taken into account. This influence was markedly reduced by choosing longer sputtering times for deeper sections thus avoiding large differences in count rate. The standard procedures for taking account of γ background, isotope lifetimes, electronic drift and small errors resulting from final section thicknesses were applied.

3. Results and discussion

Figure 1 shows a typical penetration profile together with the resolution function of the present technique. At very small penetration depths the limits of the depth resolution originating from the sputtering process have to be considered. These limits can be determined by measuring the 'penetration profile' of a non-annealed specimen. As can be seen in figure 1, this resolution function has only a little influence on the evaluation of diffusivities. Moreover, the effect is nearly the same for all measurements performed here. In particular, it is the same for both isotopes after the establishment of steady state conditions, which occurs during the sputtering of the very first monolayers. Therefore, it

has no influence on the determination of the isotope effect. Nevertheless it was taken into account.

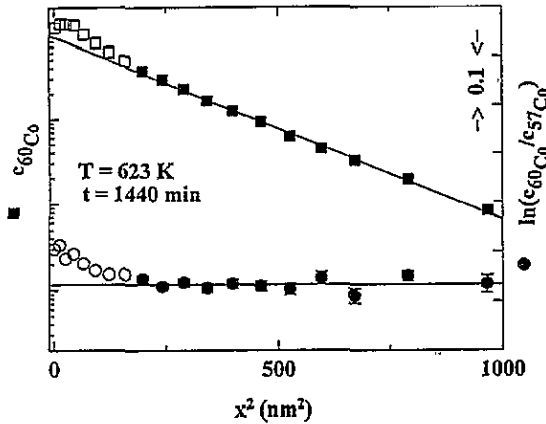


Figure 2. A typical penetration profile and the corresponding isotope-effect profile of Co diffusion into amorphous $\text{Fe}_{39}\text{Ni}_{40}\text{B}_{21}$ at $T = 623 \text{ K}$ and $t = 8.1 \times 10^4 \text{ s}$. Only filled symbols were used for the linear fits displayed. Open symbols represent data points affected by surface effects (see the text).

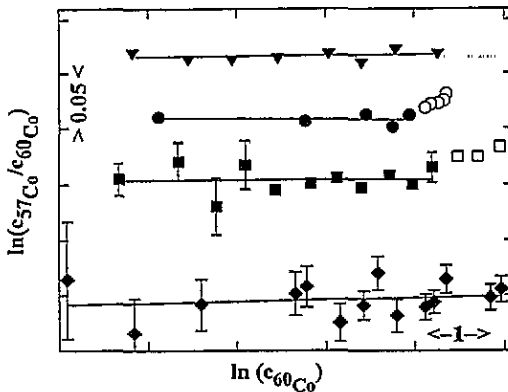


Figure 3. Isotope-effect profiles of Co diffusion in amorphous $\text{Fe}_{39}\text{Ni}_{40}\text{B}_{21}$ for different temperatures and in amorphous $\text{Fe}_{81}\text{Si}_8\text{B}_{11}$ at 649 K . From the slope of the lines the isotope effect E was calculated via equation 1. The symbols are explained in table 1. Open symbols represent data points affected by surface effects and were not taken into account.

Figure 2 shows a representative diffusion profile (left scale) and the corresponding isotope-effect profile (right scale), plotted against penetration depth squared. One notes the well-known phenomenon that the ratio of the two isotopes is more sensitive to surface effects (e.g. contamination or a thin oxide layer) than the simple profile of one isotope. Therefore, the first points were ignored in the evaluation of the isotope effect and diffusion profiles.

Figure 3 shows all measured isotope-effect profiles in $\text{Fe}_{39}\text{Ni}_{40}\text{B}_{21}$ and $\text{Fe}_{81}\text{Si}_8\text{B}_{11}$ on a $\ln(c_\alpha/c_\beta)$ against $\ln c_\alpha$ scale. The isotope effect can be calculated directly from the slope of the straight lines fitted to the data and the mass of the isotopes according to equations

(3) and (1). Equation (3) follows from equation (2) and reads

$$\ln \left(\frac{c_\alpha}{c_\beta} \right) = \text{constant} - \left(\frac{D_\alpha}{D_\beta} - 1 \right) \ln c_\alpha. \tag{3}$$

The resulting E values are listed in table 1. The errors stated are the statistical errors from the least-square fits.

Table 1. Isotope effect of Co diffusion in fully relaxed amorphous Fe₃₉Ni₄₀B₂₁ and Fe₈₁Si₈B₁₁.

Alloy	T (K)	Time (min)	$E \pm \Delta E$	Symbol in figure 3
Fe ₃₉ Ni ₄₀ B ₂₁	613	1440	-0.03 ± 0.12	▼
Fe ₃₉ Ni ₄₀ B ₂₁	620	1500	0.02 ± 0.20	●
Fe ₃₉ Ni ₄₀ B ₂₁	623	1440	-0.01 ± 0.13	■
Fe ₈₁ Si ₈ B ₁₁	649	1440	-0.06 ± 0.12	◆

The data do not exhibit any temperature dependence. Therefore, an average isotope effect of $E = (-0.007 \pm 0.07)$ was calculated for Fe₃₉Ni₄₀B₂₁. Apparently, the diffusivity of Co in amorphous Fe₃₉Ni₄₀B₂₁ and Fe₈₁Si₈B₁₁ is almost independent of the isotope mass. Within the small experimental error margins no isotope effect can be detected.

The absence of an isotope effect has also been observed in the aforementioned investigations of Co diffusion in Co-rich Co-Zr glasses [10], but has never been reported in any other material. In some crystalline alloys relatively small isotope-effect values have been observed under certain conditions. Examples are fast diffusion of very dilute impurities [11] or diffusion of the minority constituent in some highly ordered alloys [18]. In these cases it is well known that diffusion is highly correlated and occurs through single-atom jumps into thermally generated vacancies. However, the vanishing pressure dependence of Co diffusion in the amorphous Fe₃₉Ni₄₀B₂₁ alloy utilized for this study [15] shows that thermally generated vacancies can be excluded as carriers of diffusion in this alloy. Moreover, due to the chemical similarity, no strong chemical interaction between the Co tracer atom and the main constituents of the alloy, e.g. Fe and Ni, is to be expected. Therefore, the present results can certainly not be explained by a highly correlated single-jump mechanism. They rather corroborate the concepts, mentioned in the introduction, of strongly cooperative rearrangement of many atoms. A cooperative diffusion mechanism is to be expected in a densely packed structure if the assistance of vacancy-like defects can be ruled out.

In a cooperative diffusion process the mass effect is strongly 'diluted' because of the participation of many atoms. A rough quantitative description is obtained by introduction of an effective mass M of all atoms, excluding the tracer atom, that contribute to the diffusion process. This yields [10]:

$$D \propto 1/\sqrt{m + M}. \tag{4}$$

Here, M has to be regarded as a weighted average quantity. Substitution of equation (4) into equation (1) results in:

$$E \cong \left(\sqrt{\frac{m_\beta + M}{m_\alpha + M}} - 1 \right) / \left(\sqrt{\frac{m_\beta}{m_\alpha}} - 1 \right). \tag{5}$$

The extremely small isotope effects in this paper suggest effective masses of the order of $M = 50 m$. With an upper limit of $E = 0.06$, M/m is at least above 15.

Such large effective masses are not physically implausible. Effective masses of the same order of magnitude have been found in localized low-frequency vibrations and relaxations at low temperatures [9, 19]. Both processes, which seem to be universal phenomena in glasses, are closely related to each other. It has been demonstrated that the number of atoms participating in localized relaxational jumps increases at higher temperatures [20] and it was proposed that the localized collective relaxations may lead to long-range diffusion at high temperatures [9, 10]. This would immediately explain the observed absence of a measurable mass dependence of diffusion. While the present results give further evidence of highly collective diffusion in structurally relaxed metallic glasses, it has to be stressed that completely different mechanisms may operate in as-quenched glasses [21].

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