Evidence of Highly Collective Co Diffusion in the Whole Stability Range of Co-Zr Glasses

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Using a radiotracer technique, we have measured the isotope effect $E = d\ln(D)/d\ln(m^{1/2})$ of Co diffusion in $\mathrm{Co}_x\mathrm{Zr}_{1-x}$ glasses for $0.31 \leq x \leq 0.86$. E is close to zero ($E = 0 \pm 0.1$) in the whole range, covering 3 orders of magnitude in the diffusivity, despite the existence of large activation volumes. These results strongly suggest a highly collective diffusion mechanism to be a quite general phenomenon in metallic glasses and point to diffusion via delocalized thermal effects at certain compositions.

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Metallic glasses are the paradigm of dense random packing and can be designed to combine properties of ordinary glasses with the ductility of metals [1,2]. They may also exhibit excellent soft-magnetic properties or corrosion resistance [3]. Recently, certain multicomponent metallic alloys were produced at low cooling rates as bulk glasses offering hosts of new applications [4,5] and sufficient stability to study the glass transition as well as the supercooled liquid state [1,2,6–9].

The thermal stability of metallic glasses with respect to structural relaxation and the equilibrium crystalline state is controlled by their diffusion behavior, which also plays a crucial role in their production. This is why diffusion in metallic glasses has been the subject of many investigations [10–19]. Nevertheless, the available results do not provide a uniform picture of the diffusion mechanism and often seem to be conflicting. Several similarities between diffusion in crystalline and amorphous metals suggests that diffusion proceeds via a single-jump mechanism analogous to vacancy diffusion in crystals. Examples are activation volumes of the order of a vacant site [20] enhancement of diffusion under irradiation [21] and void formation during interdiffusion of amorphous thin film couples [11]. On the other hand, there are also examples of vanishing activation volumes [12,22,23], and the lack of any significant isotope effect of diffusion has provided strong evidence of a highly collective mechanism involving a large number of atoms [12,24,25]. Molecular dynamics simulations suggest collective long-range diffusion of some tens of atoms to be closely related to low-frequency excitations [26], which appear to be a universal feature of topologically disordered glasses [27].

The notion of a collective diffusion mechanism in metallic glasses is also supported by extensions of the mode coupling theory, which was originally developed to describe the glass transition [28,29]. In fragile glasses such as conventional amorphous metallic alloys recent augmented mode coupling theories predict a dynamical phase transition at a critical temperature T_c somewhere above the experimental glass-transition temperature [28]. Below T_c, liquidlike diffusion should freeze in, and long-range atomic transport is envisioned as a medium-assisted highly cooperative hopping process, where whole clusters of atoms perform thermally activated transitions into new configurations [29].

So far, vanishing isotope effects have always been found in conjunction with activation volumes close to zero [12,15,23,25]. This leads to the notion that collective diffusion proceeds via a direct mechanism not involving thermal defects. On the other hand, the observed large activation volumes of the order of an atomic volume have generally been taken as indication of diffusion analogous to the vacancy mechanism in crystalline materials.

In this paper we report the results from isotope effect measurements of Co diffusion in amorphous $\mathrm{Co}_x\mathrm{Zr}_{1-x}$ alloys with the radiotracers ^{57}Co and ^{60}Co in conjunction with ion-beam depth profiling. The measurements were carried out for $0.31 \leq x \leq 0.86$ and encompass almost the whole stability range of the amorphous phase. This binary model system was chosen because its structural [30] and thermodynamical [31] properties have been the subject of many studies, including molecular dynamics simulations [32], and diffusion in the amorphous phase has been demonstrated to exhibit a huge structural dependence. The effect of structure on diffusion manifests itself in a variation of the diffusivity at constant temperature by 3 orders of magnitude (see Fig. 1) and the occurrence of activation volumes close to zero [15] and such of the order of an atomic volume [33]. Our results reported here show that, irrespective of the large variation of the diffusivity and the activation volume, the isotope effect is close to zero in the entire range. This lends strong support to the notion that highly collective diffusion is a quite general phenomenon in metallic glasses and may also involve delocalized defects.

Amorphous $\mathrm{Co}_x\mathrm{Zr}_{1-x}$ films (main impurities: <2 at. % O, <0.1 at. % Mo) of 1 μm thickness and a lateral concentration gradient of ~0.6 at. % Co/mm were prepared on sapphire substrates by sputtering in ultrahigh vacuum (UHV) as reported in [34]. The diffusion temperatures were chosen to be well below the reported crystallization temperatures [35]. Diffusion samples were used several

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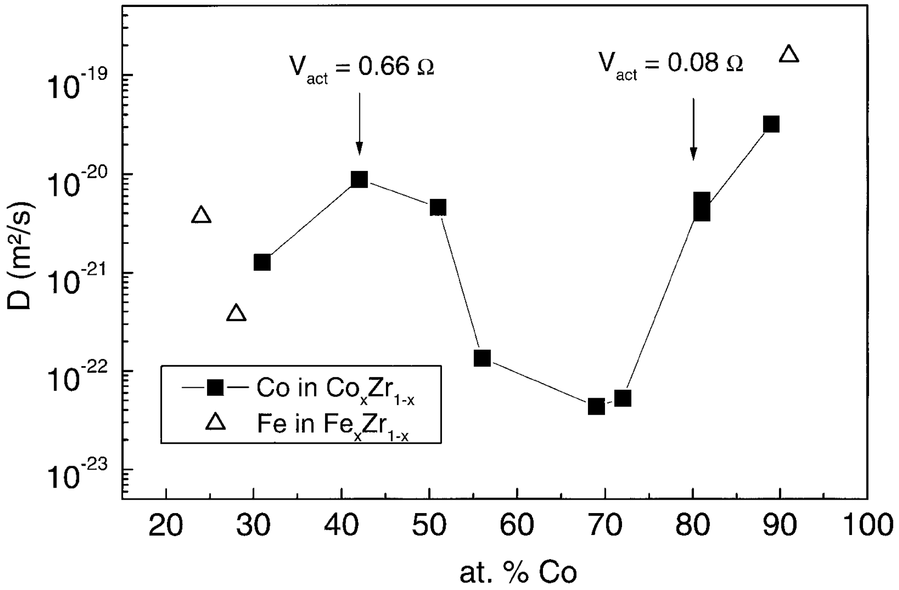

FIG. 1. Isothermal ^{57}Co diffusion coefficient vs Co concentration in structurally relaxed amorphous Co-Zr alloys at $T = 573$ K (solid squares). Data at 89 at. % Co and 81 at. % Co are from Refs. [45] and [15], respectively. Results for ^{59}Fe diffusion in Fe-Zr glasses [46] (open triangles) are shown for comparison. Here the concentration refers to Fe. Activation volumes, taken from [15,33] are indicated by arrows.

times after complete removal of the active diffusion zone by depth profiling. X-ray diffraction was carried out before and after diffusion anneals in order to rule out crystallization. Nanocrystallization, which yields diffraction patterns similar to amorphous samples, is not to be expected under the present conditions [36]. Diffusion profiles were obtained by means of ion-beam depth profiling using 600 eV Ar^+ ions as described in [37,38]. Sputter cleaning of the sample surface, tracer evaporation, and annealing were performed *in situ* in a UHV chamber ($\sim 1 \times 10^{-5}$ Pa). The area deposited with the radiotracer was 6 mm in diameter. At this diameter the lateral concentration gradient proved to be small enough not to affect the evaluation of the diffusivities within error margins of $\pm 20\%$.

The diffusion coefficients in Fig. 1 were determined from the resulting penetration profiles employing the thin-film solution of Fick's second law,

$$c(X) = \text{const} \exp(-X^2/4Dt) . \qquad (1)$$

Here c is the tracer concentration, which is proportional to the tracer activity, t is the annealing time, and X is the penetration depth. The details of the evaluation of the diffusivities and plots of the penetration profiles are given in [39]. In the present context we are concerned only with the isotope effect which has been measured at different alloy compositions and temperatures given in Table I. The moderate temperature variation is not expected to have any significant influence on the isotope effect [8,25] and was chosen only because of the large variation of the diffusivity with composition and the limited minimum penetration depth imposed by the experimental boundary conditions. With one exception, all samples were preannealed for structural relaxation. Details of the composition-dependent preannealing treatments are given in [39]. The isotope effect profiles are depicted in Fig. 2.

The isotope effect E is defined as

$$E = \frac{D_\alpha / D_\beta - 1}{\sqrt{m_\beta / m_\alpha} - 1} , \qquad (2)$$

where D_i and m_i are the diffusivity and mass of isotope i, respectively. Simple rearrangement of Eq. (1) yields

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

The isotope effects given in Table I were thus determined from the slopes of linear fits to the data in Fig. 2 by applying Eqs. (2) and (3). We note that E depends only on the isotope diffusivity ratios. Therefore, absolute errors in D_i, e.g., from uncertainties in the measurement of sputter rate and temperature, have no effect [24,25]. The error in the isotope effect values given in Table I is conservatively estimated as $< \pm 0.1$.

TABLE I. Isotope effects determined from the profiles in Fig. 2. The average value is $E = (0.016 \pm 0.06)$.

Concentration	Annealing temperature (K)	E
$Co_{31}Zr_{19}$	633	0.02(1)
$Co_{51}Zr_{49}$	573	0.11(6)
$Co_{56}Zr_{44}$	623	−0.01(1)
$Co_{69}Zr_{31}$	723	0.01(1)
$Co_{72}Zr_{28}$	637	0.07(1)
$Co_{81}Zr_{19}$	573	0.0(1)
$Co_{86}Zr_{14}$	628	−0.09(7)

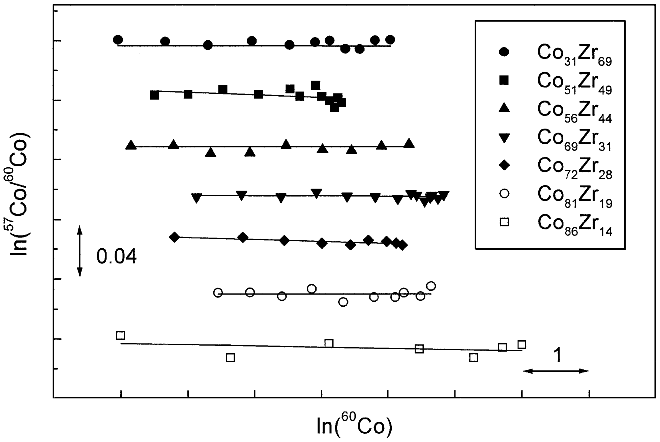

FIG. 2. Isotope effect profiles of Co diffusion in structurally relaxed amorphous Co_xZr_{1-x} alloys at different values of x. Only the sample at $x = 0.69$ was in the as-quenched state. The activity ratio of ^{57}Co and ^{60}Co is plotted vs the ^{60}Co activity on a logarithmic scale.

Obviously, for all compositions and temperatures, the isotope effect vanishes. This suggests a highly collective diffusion mechanism in the whole concentration range in accordance with the above-mentioned theoretical expectations and computer simulations. In these terms the (almost) vanishing isotope effect is the result of the strong dilution of the ordinary $m^{-1/2}$ mass dependence of the attempt frequency by coordinated hopping of a large number of atoms. Consistent with the results from molecular dynamics simulations [26,32] and the notion of a connection between the local low-frequency vibrations and long-range diffusion [26], the present low isotope effects suggest the number of atoms to be well above ten. This is also consistent with results from earlier isotope effect measurements in Co-rich Co-Zr alloys [25]. So far, however, these low isotope effects have always been interpreted in terms of a direct diffusion mechanism not involving thermal defects. This conclusion was drawn from the fact the almost-vanishing isotope effects coincided with almost-zero activation volumes [12,23].

In contrast, observations of activation volumes of the order of an atomic volume in certain systems were usually interpreted as being indicative of a diffusion mechanism analogous to the single-jump vacancy mechanism in crystals [16,20]. The present experiments, however, indicate that an activation volume of the order of an atomic volume does not necessarily imply a vacancy-mechanism-like single-jump diffusion mechanism, which should have an isotope effect of the order of unity. A mechanism consistent with a vanishing isotope effect and a large activation volume is diffusion via delocalized thermal defects. It is interesting to note that mechanisms based on delocalized thermal defects have been proposed before [17,21,40,41]. A well-known example of the notion of delocalized defects is the spread-out free volume within the free-volume approach, which was originally applied to metallic glasses by Spaepen *et al.* [40] and has recently been revived based on results from a novel nuclear magnetic resonance technique [9].

The vanishing isotope effect in the as-quenched state will be discussed elsewhere in connection with other results on the time dependence of diffusivity and isotope effect during structural relaxation and on the effect of quenched in-excess volume on diffusion [42]. Here we note only that, different from earlier results [43] in a metal-metalloid glass, we have no indications of single-atom jumps in the as-quenched state.

In conclusion, the present results strongly suggest that collective diffusion is a quite general phenomenon in metallic glasses which, in particular, is not restricted to a direct mechanism but can also occur in connection with activation volumes of the order of an atomic volume. This lends strong support to the notion of delocalized thermal defects. Finally, we note that very small isotope effects [8] in combination with large activation volumes [44] have also been observed in the deeply supercooled liquid state of a bulk metallic glass. This provides further evidence that deeply supercooled liquids behave like glasses, i.e., solidlike, and that viscous flow is frozen below a critical temperature well above the calorimetric glass-transition temperature.

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