Mass Dependence of Diffusion in a Supercooled Metallic Melt

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The isotope effect $E = (D_\alpha/D_\beta - 1)/(\sqrt{m_\beta/m_\alpha} - 1)$ of cobalt diffusion in the deeply supercooled melt of the metallic alloy $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ has been measured employing the radiotracers ^{57}Co and ^{60}Co. The isotope effect is very small, $E = 0.09 \pm 0.03$, and exhibits no significant temperature dependence in a range up to 120 K above the calorimetric glass transition temperature T_g, encompassing almost 3 orders of magnitude in the diffusivity. This result suggests that long-range diffusion in the deeply supercooled melt is not mediated by viscous flow but rather proceeds by collective hopping processes involving about ten atoms. [S0031-9007(98)06275-9]

PACS numbers: 66.10.Cb, 66.30.Fq, 64.70.Dv

Atomic transport in liquids and glasses has been the subject of many theoretical and experimental investigations, particularly in connection with the glass transition [1,2]. Diffusion in ordinary liquids at high temperatures is well understood. In this hydrodynamic regime all atoms contribute continuously to the mean square atomic displacement, and diffusion takes place via viscous flow, as described by the Stokes-Einstein relation [3]. Microscopically, transport in the hydrodynamic regime is governed by uncorrelated binary collisions of atoms. Kinetic theories for a simple liquid [3,4] predict the following mass and temperature dependence of the diffusivity D:

$$D \propto \frac{1}{\sqrt{m}} T^n, \tag{1}$$

where m is the atomic mass and n is close to 2 according to molecular dynamics simulations [1] and experiments [5]. Upon supercooling a liquid or melt the viscosity increases markedly because, due to the increase in density, atoms are more and more trapped in their nearest-neighbor "cages" for times much longer than the vibration time. According to the mode coupling theory [6] this cage effect causes viscous flow to freeze in at a critical temperature T_c. Below T_c, which is typically some 20% above the caloric glass transition temperature T_g [7], long-range diffusion in the supercooled liquid is expected to occur only via thermally activated hopping processes. Molecular dynamics simulations have shown the transition from viscous flow at high temperatures to hopping in the glassy state [8–10]. The coexistence of both processes was observed in a certain temperature range in the supercooled liquid state. Moreover, computer simulations as well as neutron scattering [11] have confirmed the existence of a critical temperature above T_g, where the decay of density correlations slows down drastically.

Whereas generally hopping in crystalline solids is a single-atom jump process [12], recent extensions of the mode coupling theory to the glassy state envision hopping in glasses as a highly cooperative medium-assisted process [13]. Highly collective hopping processes have indeed been observed in molecular dynamics simulations [10,14,15]. These simulations reveal chainlike displacements involving some ten atoms, which are suggested to be closely related to the well known low frequency excitations in glasses [14]. While, depending on the alloy composition, single-atom jumps were also observed [10] and cannot be ruled out in general for diffusion in metallic glasses [16], isotope effect measurements have confirmed the participation of some ten atoms in an elementary diffusion step in several metallic glasses [17–19]. One defines the isotope effect parameter E as

$$E_{\alpha,\beta} \equiv \frac{D_\alpha/D_\beta - 1}{\sqrt{m_\beta/m_\alpha} - 1}, \tag{2}$$

where α and β denote different isotopes. A highly collective jump process leads to a very small isotope effect since the contribution of the individual mass is diluted. On the other hand, the $1/\sqrt{m}$ mass dependence of the diffusivity in relationship (1) for viscous flow in ordinary liquids at high temperatures yields $E = 1$. Isotope effect measurements [5] of self-diffusion in liquid Sn far above the melting point T_m, have indeed revealed an E value of the order of unity confirming the notion of essentially uncorrelated single-particle motion. Upon lowering the temperature the isotope effect was found to decrease from $E = 0.7$ at 568 K above T_m to about 0.5 near T_m, indicating deviation from simple uncorrelated binary collisions already in the ordinary liquid near the melting point.

Isotope effect measurements in supercooled liquids have not yet been carried out because of experimental difficulties. Recent molecular dynamics simulations of Zr-Cu glasses have shown that low frequency excitations and hopping of groups of atoms are not restricted to the glassy state but also occur well above the glass transition

[20]. This should be reflected in a very small isotope effect. Meanwhile, the new bulk metallic glasses offer the opportunity to measure diffusion and its mass dependence in a deeply supercooled metallic melt because they are stable against crystallization on experimentally relevant time scales at temperatures well above the glass transition [21,22].

In this Letter we report isotope effect measurements of Co diffusion in the supercooled melt of the bulk metallic glass $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$. To the best of our knowledge these are the first measurements of the mass dependence of diffusion in a supercooled melt or liquid.

The glass transition temperature T_g, determined by differential scanning calorimetry at a heating rate of 2 K/s, is 596 K [23]. The experiments were performed in the temperature range of 633–713 K. This corresponds to the deeply supercooled regime far below the melting temperature of $\approx$1050 K [24]. The onset of crystallization imposes an upper temperature limit. Samples, cut from cylindrical amorphous ingots 10 mm in diameter into slices of $\approx$1 mm thickness, were polished mirrorlike on one side. The diffusing species chosen were the radiotracers ^{57}Co and ^{60}Co. They can be regarded as probes of the self-diffusion of the Ni component of the alloy, since Ni diffusivities [25] in the alloy are almost equal to the Co diffusivities reported in this Letter as expected from the similarity of both elements. An isotope mixture with an activity of typically 50 kBq, corresponding to less than a monolayer of Co, was deposited onto the polished samples. Sputter cleaning of the sample surface prior to tracer deposition, tracer evaporation, and annealing were performed *in situ* in ultrahigh vacuum ($\approx 10^{-6}$ Pa). X-ray diffraction was employed after the diffusion anneals to check for crystallization. Diffusion profiles were obtained by serial sectioning of the samples using ion-beam sputtering by means of 600 eV Ar ions [26]. The concentration of the isotopes in each section was determined by means of a Ge detector counting the intensities of the 122, 136 keV (^{57}Co) and 1.17, 1.33 MeV (^{60}Co) γ lines. The statistical errors in counting were minimized by using, e.g., large tracer activities, long integration times, made possible by excellent drift stability of the present equipment (DSG *PGC* 4019, Ortec 672), elaborate shielding against background radiation, and an increase in section thickness at lower concentrations.

The resulting penetration profiles are shown in Fig. 1. Under these conditions the Co concentration $c(x,t)$ at the depth x is given by the thin film solution [12] of Fick's second law

$$c(x,t) = \mathrm{const}\exp\left(\frac{-x^2}{4Dt}\right),\qquad (3)$$

where t denotes the annealing time and D the diffusion coefficient, which can be extracted from the slope of the linear portion of the penetration profiles and the annealing time. The very first data points were affected by surface
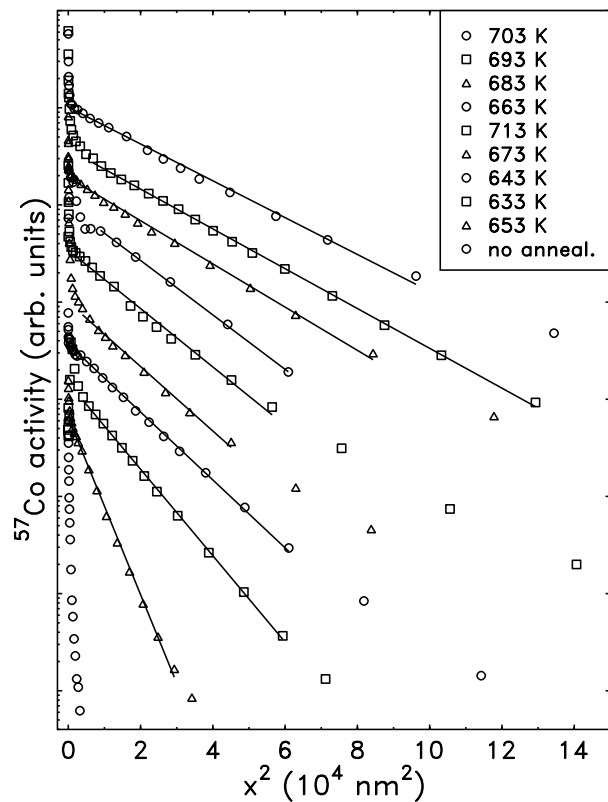
FIG. 1. Penetration profiles of ^{57}Co diffusion for different temperatures. The ^{57}Co activity is plotted on a logarithmic scale vs the square of the penetration depth.

effects [27] and were not taken into account. Data points at large penetration depths are influenced by background activity [26] and were neglected, too.

The temperature dependence of Co diffusion is shown in an Arrhenius plot in Fig. 2. The data can be fitted by a straight line over the whole temperature range yielding an activation energy of $Q = 3.4 \pm 0.1$ eV and a preexponential factor of $D_0 = 1.5 \times 10^{(8\pm0.8)}$ m^2/s. The sample referring to the highest annealing temperature of 713 K was partially crystallized and was not taken into account, although the very small isotope effect (Table I) indicates that effects from diffusion in the crystalline phase, where much larger isotope effects are expected [28], are negligible. Results for Be and Al diffusion in the amorphous alloy are shown for comparison [29,30]. Only the Al data originate from direct tracer measurements by means of secondary ion mass spectrometry. The Be diffusivities are interdiffusion coefficients [12], obtained from a Be/amorphous-alloy couple, which do not necessarily reflect the tracer diffusion coefficient of Be. While our Co diffusivities are in good agreement with the aforementioned Ni radiotracer values [25], and the much smaller diffusivities of Al can be attributed to the significantly larger atomic size of Al, the intersection of the Be and Co diffusivities in Fig. 2 is unexpected. Theoretical considerations and computer simulations [10] rather predict that the diffusion coefficients of different components
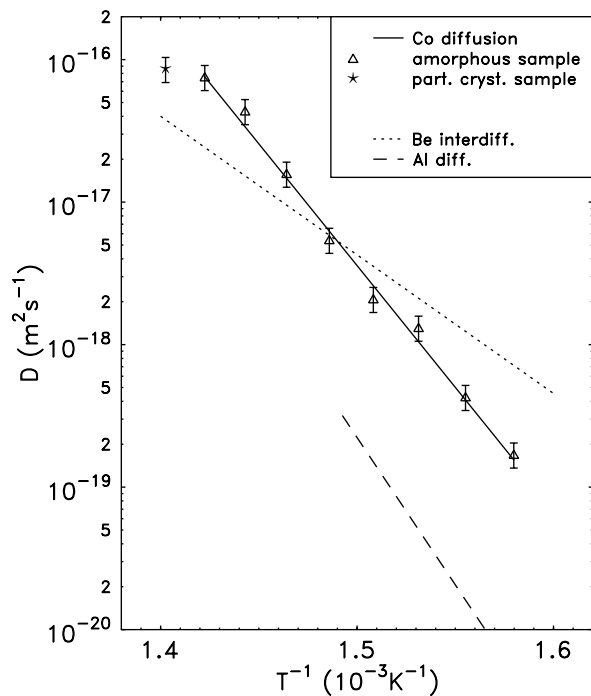
FIG. 2. Arrhenius plot of the ^{57}Co diffusivities. For comparison data for Al tracer diffusion from Ref. [29] and for Be interdiffusion from Ref. [30] in the same alloy are shown.

approach each other with increasing temperature and become quite similar in the viscous flow regime, where diffusion and viscosity are related by the Stokes-Einstein relation.

Moreover, a downward curvature of the Arrhenius plots is expected above the glass transition and a crossover from the strong temperature dependence observed in the supercooled liquid state to the weak power-law dependence, described by Eq. (1), in the hydrodynamic regime [10,24]. Apparently, this curvature cannot yet be resolved experimentally in the available temperature range. Since any rise in temperature above the glass transition is accompanied by pronounced structural changes, which are reflected in an increase in free volume, for instance, and considerable enhance diffusion, Q values should be regarded as effective quantities that do not reflect actual barrier heights [31,32].

TABLE I. Overview of Co diffusion data.

T (K)	t (s)	$D(10^{-18}$ m^2/s)	$E \pm \Delta E$
633	14 400	0.17	0.09 ± 0.04
643	7200	0.43	0.12 ± 0.03
653	900	1.3	0.13 ± 0.03
663	1800	2.2	⋯
673	600	5.5	0.01 ± 0.15
683	307	16	0.15 ± 0.04
693	121	44	0.10 ± 0.03
703	76	76	0.07 ± 0.05
713	42	86	0.03 ± 0.05

The mass dependence of Co diffusion was studied by determining the isotope effect parameter E. In Fig. 3 the activity ratio of ^{57}Co and ^{60}Co is plotted versus the ^{57}Co activity on logarithmic scales. By means of the thin film solution (3) one obtains

$$\ln\left(\frac{c_\alpha}{c_\beta}\right) = \text{const} - \left(\frac{D_\alpha}{D_\beta} - 1\right)\ln c_\alpha . \qquad (4)$$

Hence, the slope of the graphs directly yield $D_\alpha/D_\beta - 1$, and E can be calculated from Eq. (2). The resulting E values are shown in Table I. Errors given represent the statistical errors of the linear fits in Fig. 3. The total errors are estimated as less than twice these statistical errors. One notes that the isotope effect is very small in the whole temperature range and exhibits no significant temperature dependence. It can therefore be represented by an average value of $E = 0.09 \pm 0.03$.

The very small isotope effect clearly shows that the diffusion mechanism in the strongly supercooled melt is completely different from uncorrelated single-atom motion in ordinary viscous flow, where E would be of the order of unity, as discussed above. The very weak mass dependence rather suggests that the influence of an individual mass on the long-range diffusivity is strongly diluted because of the participation of a large number of atoms in the diffusion process. Judging from the magnitude of the
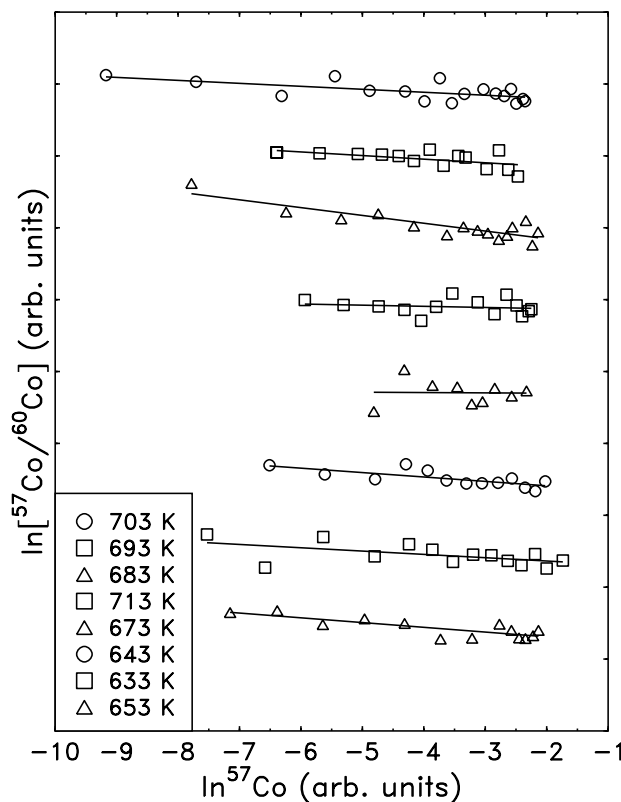

FIG. 3. Activity ratio ^{57}Co/^{60}Co vs the activity of ^{57}Co on logarithmic scales for different temperatures. The division of the ordinate is 0.05. The isotope effect E can be extracted from the slope of the straight lines according to Eq. (4).

measured isotope effects, diffusion in the deeply super-cooled regime between the critical temperature of the mode coupling theory and the caloric glass transition temperature seems to be similar to diffusion in the glassy state [17–19], i.e., a highly cooperative hopping process. This lends support to the aforementioned augmented mode-coupling theory [13] and corroborates the results from the recent molecular-dynamics simulations [20] in the super-cooled liquid regime, alluded to above, which reveal chain-like displacements of groups of atoms.

Attributing the very small measured isotope effects to mass "dilution" caused by coordinated hopping of groups of atoms, as suggested by the computer simulations, we can immediately estimate the number of atoms partici-pating in the jump process. In these terms the $1/\sqrt{m}$ mass dependence of the diffusivity for single-atom jumps, originating from the corresponding mass dependence of the attempt frequency (harmonic vibrations), has to be replaced by introduction of an effective mass M of all atoms, excluding the tracer atom, that participate in the jump process [18,33]:

$$D \propto 1/\sqrt{m + M}. \tag{5}$$

With the present value of $E = 0.09$ the number M/m of atoms hopping jointly is of the order of 10. This value is in the range of isotope effects measured for Co diffusion in conventional metallic glasses below T_g [17–19].

In conclusion, the very small isotope effect measured in this work suggests that collective hopping and not viscous flow governs long-range diffusion in the supercooled melt in a considerable temperature range above the calorimetric glass transition temperature. Apparently, the barriers imposed on diffusing atoms by their nearest neighbors are stable on the time scale of diffusion jumps. Hopping is a highly cooperative process involving about ten atoms. This corroborates recent extensions of the mode coupling theory predicting the freezing in of viscous flow at a critical temperature T_c and medium-assisted cooperative hopping of groups of atoms below T_c. The lack of any indication of an increase in the isotope effect in the investigated temperature range up to 120 K above the calorimetric glass transition temperature suggests T_c to be located well above this range.

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