# Atomic Diffusion in the Supercooled Liquid and Glassy States of the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ Alloy

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The self-diffusivity of Be in the bulk metallic amorphous alloy $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ is investigated. Below the glass transition temperature the data suggest a single atomic jump diffusion behavior of Be. By taking into account the change in configurational entropy due to the glass transition, we explain the mechanism for diffusion of Be in the supercooled liquid state (i.e., above the glass transition) of $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ by single atomic jumps in a slowly changing configuration of neighboring atoms.

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Diffusion phenomena in metallic glasses have been investigated in a large variety of binary and ternary metallic amorphous alloys [1]. The main objectives of these investigations were to reveal the nature of atomic transport processes in metallic glasses, as well as to understand the influence of diffusion processes on their thermal stability. So far, the poor thermal stability of conventional metallic glasses with respect to crystallization has restricted measurements of diffusion and other physical properties to the solid state (SS), while the supercooled liquid state (SLS) of the alloys (i.e., the state above the glass transition) was not accessible. Recently, novel classes of glass-forming systems with stability over a large supercooled liquid region were found [2,3]. The high thermal stability of these alloys with respect to crystallization above the glass transition temperature $T_g$ [4] provides an experimental time scale which is sufficient to perform measurements of atomic transport phenomena like diffusion and viscosity [5] in the supercooled liquid state.

In this Letter we show that it is possible to investigate diffusion in the SLS of the bulk metallic amorphous alloy $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$ and present results on the self-diffusion of Be in this system below and above $T_g$. Since the supercooled liquid is highly viscous in the temperature regime studied, we assume that convection effects on the atomic transport properties need not be considered. Beryllium, as the smallest and possibly fastest diffusing component, was chosen for the experiments on diffusion in the SLS of a metallic glass. Because no radioactive Be tracers are available we chose elastic backscattering (EBS) for the analysis of Be concentration depth profiles.

Disks of bulk amorphous $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ samples [3] with a diameter of 5 mm and thickness of 1 mm were polished mechanically and electrochemically. The sample surfaces were sputter cleaned with 4 keV $Ar^+$ ions to remove the surface oxide which could act as a diffusion barrier. Finally, a Be layer with a thickness of about 1 $\mu$m was deposited at room temperature by ion beam sputtering of Be. Both cleaning and Be deposition were carried out under UHV conditions (base pressure $10^{-10}$ mbar) to prevent reoxidation of the sample surfaces.

Each sample was cut into two pieces, one of these being heat treated for different times at the same temperature and the other serving as a reference sample. The annealing was performed in a differential scanning calorimeter or in a rapid thermal annealing furnace. After each heat treatment the samples were analyzed by x-ray diffraction and/or transmission electron microscopy to confirm their amorphous structure.

EBS analysis of the Be concentration depth profiles was performed with the Caltech tandem electrostatic accelerator using 6.5 MeV $^4He^{2+}$ ions and typical beam current densities of about 10 nA/mm$^2$. The backscattered ions were collected at a backscattering angle of 177°. The elastic backscattering cross section of Be for 6.5 MeV $\alpha$ particles at this angle is about 25 times the Rutherford cross section, and depends only slightly on energy [6].

In order to calculate effects of a finite energy resolution of the electronics, interface roughness, and energy straggling, each measurement of a heat-treated sample was preceded by the analysis of its untreated reference sample. All effects can be successfully taken into account by assuming a simple Gaussian signal broadening, as demonstrated in Fig. 1(a) for a reference sample. Diffusion of Zr, Ti, Cu, and Ni into the Be layer was not observed within the experimental precision. The low energy tails of the Be backscattering signals com-

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ing from regions with a Be content near 22.5 at. % were used for the quantitative analysis of Be self-diffusion in the alloy $\mathrm{Zr}_{41.2}\mathrm{Ti}_{13.8}\mathrm{Ni}_{10}\mathrm{Cu}_{12.5}\mathrm{Be}_{22.5}$. In Fig. 1(b) the backscattering data of a heat-treated sample corresponding to Fig. 1(a) are shown. The diffusion profile fit matches the data for low Be content.

Diffusion in the solid state of rapidly quenched conventional metallic glasses is known to be sensitive to the relaxation state of the samples. In a nonrelaxed sample the diffusivity drops as a function of time due to structural relaxation and annealing of excess free volume. It approaches a constant value when the sample is fully relaxed [7]. It is thus essential to check for relaxation effects in evaluating diffusion data. Figure 2 shows that the self-diffusivity $D_{\mathrm{Be}}$ of Be does not depend on the duration of the heat treatment within the experimental error, showing that no significant relaxation effects occur.

Figure 3 shows an Arrhenius plot of the $D_{\mathrm{Be}}$ data. The data can be divided into two subsets. The first subset for temperatures from 533 to 613 K fits an Arrhenius law $D_{\mathrm{Be}}(T) = D_0 \exp(-Q/k_B T)$ with $D_0 = 1.8 \times 10^{-11}$ m$^2$/s and $Q = 1.05(8)$ eV atom$^{-1}$. The second subset for the temperatures from 623 to 663 K also fits an Arrhenius law, but with remarkably different values, $D_0 = 1.1 \times 10^{+17}$ m$^2$/s and $Q = 4.47(2)$ eV atom$^{-1}$. The errors of the $D_0$ values can be given by multiplicative factors 5.3 ($T < 623$ K) and 15.8 ($T \geq 623$ K), respectively, Both Arrhenius fits are shown in Fig. 3.

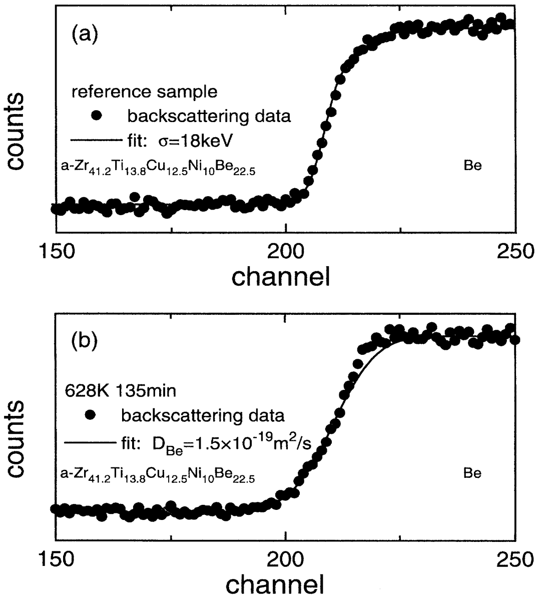

FIG. 1. (a) Backscattering data of an as prepared $\mathrm{Zr}_{41.2}\mathrm{Ti}_{13.8}\mathrm{Ni}_{10}\mathrm{Cu}_{12.5}\mathrm{Be}_{22.5}$/Be interface (solid circles). All signal broadening effects can be taken into account by a simple Gaussian broadening function with standard deviation $\sigma = 18$ keV (solid line). (b) Backscattering data of the interface corresponding to (a) after 135 min heat treatment at 628 K (solid circles). The Be concentration profile can be fitted for low Be content, assuming the above signal broadening and $D_{\mathrm{Be}} = 1.5 \times 10^{-19}$ m$^2$/s (solid line).

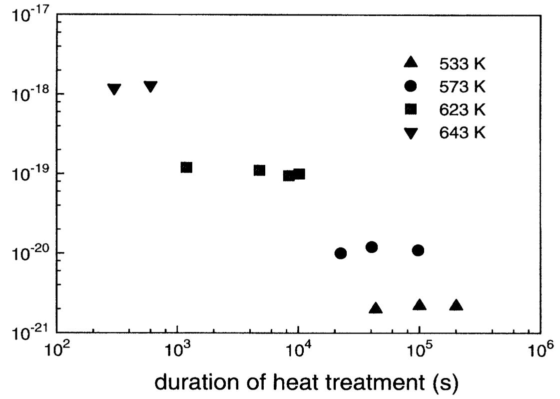

FIG. 2. Self-diffusivity of Be in $\mathrm{Zr}_{41.2}\mathrm{Ti}_{13.8}\mathrm{Ni}_{10}\mathrm{Cu}_{12.5}\mathrm{Be}_{22.5}$ as a function of the duration of heat treatment at 533, 573, 623, and 643 K.

The change in the temperature dependence of $D_{\mathrm{Be}}$ at about 623 K is associated with the glass transition. We assume that within the time scale of our experiments the glass temperature is fixed and that the alloy undergoes the glass transition at the very beginning of the isothermal heat treatment. Below 623 K the amorphous samples are in the SS, and above they are in the SLS. $D_{\mathrm{Be}}$ increases by 2 orders of magnitude over 40 K above $T_g$. Diffusion data above 663 K were not accessible due to crystallization.

Arrhenius behavior of diffusion is well known in the SS of conventional metallic glasses. It indicates thermally activated processes with a relatively narrow distribution of activation energies. However, $D_0$ values observed for self-diffusion and impurity diffusion in relaxed solid metallic glasses vary over 10 orders of magnitude

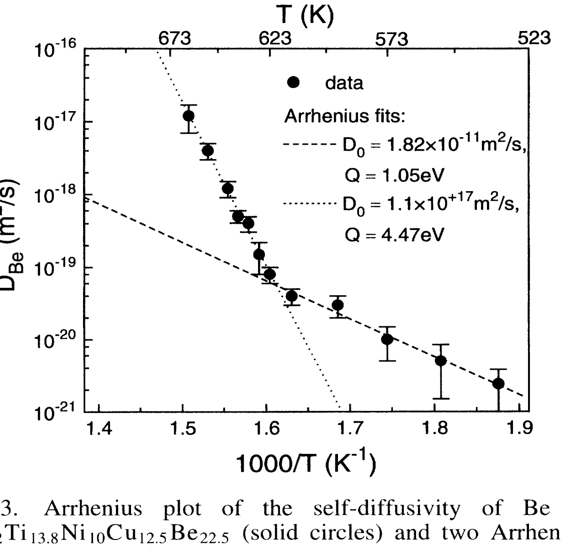

FIG. 3. Arrhenius plot of the self-diffusivity of Be in $\mathrm{Zr}_{41.2}\mathrm{Ti}_{13.8}\mathrm{Ni}_{10}\mathrm{Cu}_{12.5}\mathrm{Be}_{22.5}$ (solid circles) and two Arrhenius fits to the data (lines).

[7,8] . Since this is not consistent with an indirect mechanism of diffusion mediated by vacancylike defects, it has been suggested that diffusion takes place via a direct mechanism involving thermal fluctuations of diffuse volumetric defects [7]. In this context, diffusive single atom jumps seem possible only for small atoms (like Be) or, for larger atoms, in a loosely packed amorphous structure. In the case of large atoms in dense amorphous structures, diffusion requires a cooperative motion involving a cluster of neighboring atoms [7]. Faupel and co-workers have demonstrated such cooperative effects and report a minimum cluster of ten atoms involved in the diffusion of Co in amorphous $Co_{76.7}Fe_2Nb_{14.3}B_7$ [9]. The activation energy of this cooperative motion contains no contribution from the formation enthalpy of defects (as in crystals) and can be identified with a migration enthalpy $H_M^{SS}$. The large number of atoms involved in the cooperative motion is reflected in high $H_M^{SS}$ or $Q^{SS}$ values. In the same way, $D_0^{SS}$ is not linked to a formation entropy of defects, but only to a migration entropy $S_M^{SS}$. The relevant expressions here are

$$\begin{aligned} D^{SS}(T) &= D_0^{SS} \exp\left(-\frac{H_M^{SS}}{k_B T}\right), \\ D_0^{SS} &= g\langle x^2\rangle \nu_0 \exp\left(\frac{S_M^{SS}}{k_B}\right), \end{aligned} \qquad (1)$$

with $g$ a geometric factor, $\langle x^2\rangle$ the mean square of the jump distance, and $\nu_0$ the jump attempt frequency. Thus a small $D_0$ value indicates a small positive or even negative migration entropy.

The small values $Q^{SS} \approx 1.1$ eV and $D_0^{SS} \approx 1.8 \times 10^{-11}$ m$^2$/s for diffusion in the SS suggest a single jump motion of the small Be atoms (atomic radius 0.111 nm) in the alloy $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$. The $Q$ and $D_0$ values for Be self-diffusion in the SLS, as suggested by the Arrhenius fit, are extremely high. According to the above arguments, $Q^{SLS} \approx 4.5$ eV might reflect a highly cooperative motion of numerous atoms in the SLS. The increase of $D_0$ (over 28 orders of magnitude) cannot be understood by a change of the factors $g\langle x^2\rangle\nu_0$ in Eq. (1). In the SLS, $\langle x^2\rangle$ and $\nu_0$ may change with respect to the SS, but the main effect must be explained by a substantial increase of the second exponential term in Eq. (1) due to the glass transition.

An interpretation of the diffusion process that is rather different from the above cooperative behavior arises if we take into account the temperature dependent entropy change $\Delta s^{SLS}(T)$ per atom due to the glass transition of the alloy $Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}$. Above, but near $T_g$, this can be approximated by a linear term in a series expansion as

$$\Delta s^{SLS}(T) \approx \frac{\Delta c_p(Tg)}{N_A T_g}(T - T_g) + \text{(higher order terms)}, \qquad (2)$$

where $\Delta s^{SLS}(T)$ is the change of entropy per atom of the undercooled liquid above the glass transition where the system samples a greater portion of configurational phase space. We assume that changes of electronic and vibrational contributions to $\Delta s^{SLS}(T)$ can be neglected near $T_g$ so that $\Delta s^{SLS}(T)$ is mainly a configurational ("communal") entropy. $\Delta c_p(T_g)/T_g$ is the difference in the slope at $T_g$ of the entropy versus temperature functions of the undercooled liquid and the glassy states, and $N_A$ is Avogadro's number. To estimate the effect of the glass transition on the diffusivity, we assume that the relation (1) for a direct thermally activated diffusion mechanism still holds in the SLS, and that a diffusing Be atom is influenced by the liquidlike behavior of $N$ nearest and possibly next-nearest neighbors. We account for the enhanced configurational entropy related to this liquidlike cell of $N$ atoms by adding a factor according to Eq. (2) to the migration entropy of the SS in Eq. (1):

$$D_0^{SLS}(T) = g^{SLS}\langle x^2\rangle^{SLS}\nu_0^{SLS} \exp\left(\frac{S_M^{SS} + N\Delta s^{SLS}(T)}{k_B}\right). \qquad (3)$$

One can approximate $\Delta c_p(T_g)$ as the specific heat capacity difference at $T_g$ of the SLS and the crystalline states. Experimentally, it has been found that $\Delta c_p(T_g)/N_A$ is $2.9k_B$ atom$^{-1}$ [10]. Equations (1) and (3) then result in

$$D^{SLS}(T) = D_0^{SLS} \exp\left(N\, 2.9\, \frac{T - T_g}{T_g}\right) \exp\left(-\frac{H_M^{SLS}}{k_B T}\right), \qquad (4)$$

combining all temperature independent quantities to $D_0^{SLS}$.

By fitting the experimental diffusion data for $D_{Be}$ in the SLS state above $T_g$ using Eq. (4), one obtains values of $D_0^{SLS} = 1.4 \times 10^{-11}$ m$^2$/s, $N = 22(1)$, and $H_M^{SLS} = 1.020(5)$ eV atom$^{-1}$ for the three fitting parameters. The quality of the fit is as good as the Arrhenius fit mentioned earlier. Note that the preexponential factor and the migration enthalpy obtained ($D_0^{SLS}$,$H_M^{SLS}$) are almost identical to those found for the Arrhenius law below $T_g$ ($D_0^{SS}$, $H_M^{SS}$), so that within these considerations neither a high migration enthalpy in the SLS nor a change of $D_0$ at $T_g$ have to be explained.

The above calculations suggest the following picture for diffusion of Be in the SLS. The time scale for a diffusive atomic jump is of the order $\nu_0^{-1}$. It is much shorter than the time scale for atomic rearrangements in the viscous supercooled liquid leading to viscous flow (which is of the order of seconds near $T_g$). Thus a Be atom effectively moves in a rigid cage of neighboring atoms, just as in the SS. This cage is quite similar as in the SS and leads to the same preexponential factor and migration enthalpy, still indicating a single atomic jump behavior. However, the much slower atomic rearrangements of the liquidlike cell of $N$ neighboring atoms offer a larger number of configurations than in the SS that can enable the diffusive motion. This larger number of configurations is reflected in the additive

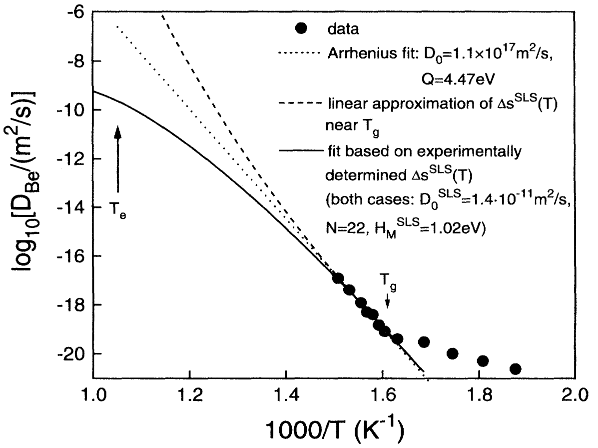

FIG. 4. Diffusivity data with Arrhenius and modified Arrhenius fit according to Eq. (4) and $D_{\mathrm{Be}}(T)$ based on the full experimentally determined $\Delta s^{\mathrm{SLS}}(T)$. $T_g$ is the glass transition temperature and $T_e$ the eutectic temperature of the alloy.

entropy term $N\Delta s^{\mathrm{SLS}}(T)$ of Eq. (3). The independence with respect to the time of the diffusive jumps and the slow atomic rearrangements justifies the simple addition. The fitting result $N \approx 22$ actually indicates that only the changing configurations of the nearest and probably some of the next-nearest neighbors of a Be atom influence the diffusive process. In contrast to the cooperative diffusion behavior in the SS of metallic amorphous alloys [9], this supporting movement of neighboring atoms happens on a different time scale and requires no thermal activation. The enhanced temperature dependence of the diffusivity of Be in the SLS of $\mathrm{Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}}$ is not in fact due to a higher activation energy, but rather to the increasing contribution of the liquid communal entropy with temperature in the SLS. This temperature dependence can be attributed to the growing portion of phase space (especially of its momentum branch) that is probed by the liquidlike cells with increasing temperature and decreasing viscosity.

According to the above arguments, the basic effect of the glass transition on the diffusion of Be in amorphous $\mathrm{Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}}$ is the onset of additional atomic movements on a time scale that is long with respect to the duration of a single jump, but comparable with the time between two successive jumps, and short compared to the experimental time scale. Thus a Be atom probes a much larger variety of configurations of its nearest and next-nearest neighbors during diffusion in the SLS than in the SS. The related communal entropy increases distinctly with temperature, and this temperature dependent entropy term mimics a large activation energy for diffusion (if one interprets data in term of Arrhenius behavior). Also, within our analysis based on Eq. (4) (instead of an Arrhenius law) there is no need to explain a change of $D_0$ at $T_g$. It must be clarified whether these features are generally valid for diffusion in the SLS of this and other amorphous metallic systems.

The key for further checking these arguments is the extension of the diffusivity measurements to higher temperatures. To properly extend Eq. (4) to higher temperature, one must include the higher order terms in Eq. (2). Equivalently, one can use the full experimentally determined $\Delta s^{\mathrm{SLS}}(T)$ as reported in Ref. [10]. Further taking $H_M^{\mathrm{SLS}}$ to be temperature independent, one can generate the function $D_{\mathrm{Be}}(T)$ over the entire supercooled region from $T_g$ to $T_e$, the eutectic liquidus temperature. This is shown in Fig. 4 (solid curve) for comparison with the Arrhenius fit and the linear approximation of $\Delta s^{\mathrm{SLS}}(T)$. Notice that this curve gives $D_{\mathrm{Be}}(T_e) \approx 2 \times 10^{-10}\ \mathrm{m^2/s}$, a very reasonable value.

In summary, our data on the diffusion of beryllium in the amorphous alloy $\mathrm{Zr_{41.2}Ti_{13.8}Ni_{10}Cu_{12.5}Be_{22.5}}$ can be interpreted in terms of a single atomic jump diffusion mechanism, in both the solid and supercooled liquid states. The diffusivity in the supercooled liquid state can be described by a modified Arrhenius law, which reflects the effect of the onset of the atomic movements responsible for the viscous flow of the supercooled liquid above $T_g$, and is related to the communal entropy of the liquid.

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[1] J. Horvath, in *Diffusion in Solid Metals and Alloys,* edited by H. Mehrer, Landoldt-Börnstein, New Series, Group 3, Vol. 26 (Springer, Berlin, 1990), p. 437.
[2] A. Inoue, T. Zhang, and T. Masumoto, Mater. Trans. JIM **31**, 177 (1990).
[3] A. Peker and W. L. Johnson, Appl. Phys. Lett. **63**, 2342 (1993).
[4] W. L. Johnson and A. Peker, in *Science and Technology of Rapid Solidification and Processing,* edited by M. A. Otooni (to be published), p. 25.
[5] R. Rambousky, M. Moske, and K. Samwer, Mater. Sci. Forum **179-181**, 761 (1995).
[6] Y. Qiu, U. Geyer, S. Schneider, M.-P. Macht, and T. A. Tombrello (to be published).
[7] W. Frank, A. Hörner, P. Scharwächter, and H. Kronmüller, Mater. Sci. Eng. **A179/A180**, 36 (1994).
[8] S. K. Sharma, M.-P. Macht, and V. Naundorf, Phys. Rev. B **49**, 6655 (1994).
[9] F. Faupel, P. W. Hüppe, and K. Rätzke, Phys. Rev. Lett. **65**, 1219 (1990); P. W. Hüppe and F. Faupel, Phys. Rev. B **46**, 120 (1992).
[10] R. Busch, Y. J. Kim, and W. L. Johnson, J. Appl. Phys. **77**, 4039 (1995).