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Determination of self-diffusion coefficients by quasielastic neutron scattering measurements of levitated Ni droplets

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Conventional techniques to measure diffusion coefficients in liquid metals and alloys are hampered by buoyancy-driven convective fluid flow and chemical reactions of the liquids with container material. To overcome these obstacles we combined containerless processing via electromagnetic levitation with quasielastic neutron scattering. This combination allowed us to study the atomic self-motion in liquid nickel within a broad temperature range from 200 K above to more than 200 K below the melting point, in the metastable regime of an undercooled melt. Other than in liquid Sn the temperature dependence of the Ni self-diffusion coefficient is well described with an Arrhenius law.

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Processes on the atomic scale determine the physical properties of mass transport in liquids, as well as crystal growth and microstructure evolution during solidification of alloys. In this respect the knowledge of diffusion coefficients, including their temperature and concentration dependence, as well as the profound understanding of diffusion mechanisms is a necessary prerequisite for modeling of solidification processes[1–4] and, hence, to enable a successful materials design from the melt.

From the experimental side, classical diffusion experiments in liquid metals, e.g., using the long-capillary method,[5] are hampered by buoyancy-driven convective flow and chemical reactions of the melt with the capillary. For these reasons experimental diffusion data in liquid alloys are rare, the more so the larger the processing temperatures involved. Quasielastic neutron scattering (QNS) probes sample dynamics on atomic time and length scales, and therefore, the resulting data are not altered by convective flow. This enables us to derive self-diffusion coefficients on an absolute scale for liquids containing an incoherently scattering element.[6–10]

Although special thin-walled SiC (Refs. 11–13) and Al_2O_3 (Refs. 14–16) sample crucibles were used, QNS experiments have been limited so far to low melting and/or chemically fairly inert metallic systems and to temperatures close above the liquidus temperature. In order to give access to the study of refractory and chemically reactive melts, containerless processing techniques are required. The absence of a sample holder makes it not only possible to extend the accessible temperature range to high temperatures of up to 2300 K, but also into the metastable regime of the undercooled liquid several hundreds of Kelvin below the equilibrium melting point, due to the avoidance of heterogeneous nucleation at crucible walls.

To enable these investigations we designed an electromagnetic levitation (EML) device for the use with QNS. For a first measurement on the new neutron time-of-flight (TOFTOF) spectrometer at the FRM II,[17,18] we have chosen liquid Ni, which is a strong incoherent scatterer ($\sigma_i = 5.2$ barn). As there are diffusion data available for pure Ni in a thin-walled sample geometry,[14] we could verify the levitation approach, and proof that the larger thickness of the levitated samples, with its effects on multiple scattering, does not obstruct the determination of the Ni self-diffusion coefficients with high precision.

A new generation of neutron time-of-flight spectrometers provides an increase in neutron flux and signal-to-noise ratio of more than an order of magnitude. Through the combination with a compact electromagnetic levitation device[19,20] quasielastic neutron scattering on small levitated droplets is now feasible. In addition, we succeeded to develop a coil design of the EML with a large opening (8 mm) between the upper and lower parts of the coil without loss of stability in the sample positioning. This enhanced the visibility of the sample for the incoming neutron beam and enabled a nearly full coverage of the detector banks up to 20° vertical angle and thus increased the count rate by another factor of 10.

The roughly spherical, electrically conductive Ni samples, 8 mm in diameter with a mass of 2.2 g, are levitated within an inhomogeneous electromagnetic radio frequency (rf) field. As a result of the rf field, eddy currents are induced in the specimen. On the one hand, this leads to an inductive heating of the sample which allows melting of the specimen. On the other hand, the interaction of the eddy currents with the inhomogeneous magnetic field of the levitation coil leads to a force into the direction of low magnetic field strength such that gravity is compensated. The convective stirring induced by the inductive currents in combination with a large heat conductivity of the sample results in a homogenous sample temperature[21] that is measured contact-free with a two-color pyrometer. The absolute temperature is derived by gauging the measured melting temperature to the literature value for T_m(Ni) of 1726 K. The temperature of the melt is controlled via the flow of ultrapure cooling gas (He/4% H_2) which is injected by a nozzle that is installed below the sample. The addition of hydrogen gas is used to reduce oxide impurities on the sample surface. Before operation the sample chamber is evacuated and subsequently filled with 350 mbar ultrapure He/4% H_2 gas. Data acquisition times were 3 h for temperatures below the melting point, and 1 h for temperatures above the melting point.

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At TOFTOF an incident neutron wavelength of 5.4 Å gives an accessible range of momentum transfer q between 0.4 and 2.2 $Å^{-1}$ at zero energy transfer. This is well below the first structure factor maximum of liquid Ni,[20] at about 3 $Å^{-1}$ and hence scattering is dominated by incoherent contributions. A measurement of the solid sample at room temperature yields the instrumental energy resolution function that is described well by a Gaussian function with an energy resolution of $\delta E \approx 78$ μeV full width at half maximum. The absence of a sample holder in combination with a shielding of the Cu coils with a ^{6}Li containing rubber results in an excellent signal-to-noise ratio of better than 1000:1, despite the small sample size and the high temperatures involved. Measured data are corrected for background and normalized to a vanadium standard.

For incoherent scattering the scattering law $S^*(q,\omega)$ is the Fourier transform of the self-correlation function $G_s(r,t)$,[22–24] which for diffusive motion yields

$$S^*(q,\omega) = \frac{A}{\pi\hbar}\frac{Dq^2}{(Dq^2)^2+\omega^2} + b_q, \tag{1}$$

where A is an amplitude of the quasielastic signal and b_q accounts for contributions of atomic vibrations that are assumed to be constant in the fitting range of up to ±2.6 meV (Debye level). For the fitting of the measured $S(q,\omega)$ this Lorentzian function has to be convoluted with the instrumental energy resolution function.

Figure 1 displays the quasielastic signal of $S(q,\omega)$ for different temperatures and values of the momentum transfer q in a semilogarithmic representation. Spectra are well described by fits with Eq. (1).

For incoherent scattering, the width of the quasielastic line, which is indirectly proportional to the decay time of the self-correlation, is proportional to q^2 at small q values. The proportionality constant is the Ni self-diffusion coefficient

$$D = \frac{\Gamma_{1/2}(q)}{\hbar q^2}, \tag{2}$$

with $\Gamma_{1/2}(q)$ the half width at half maximum of the scattering function $S(q,\omega)$. In Fig. 2, $\Gamma_{1/2}$ is plotted versus q^2 for different temperatures. As in multicomponent glass forming alloys[6,13] this q^2 dependence holds up to about 1.5 $Å^{-1}$. At larger q values coherent scattering contributes increasingly to the signal.

From the slope of $\Gamma_{1/2}$ as function of q^2, the self-diffusion coefficient D is derived for each temperature on an absolute scale with high precision. The values for the derived Ni self-diffusion coefficients are given in Table I.

The temperature dependence of the Ni self-diffusion coefficients is plotted in Fig. 3. Also shown are results of earlier QNS measurements on liquid Ni performed in a special crucible shaping a sample geometry of a hollow cylinder with 0.6 mm wall thickness.[14] These data points are in excellent agreement with the results of the levitation experiment. This shows that the increase in sample thickness and the corresponding increase in multiple scattering events do not alter the determination of the diffusion coefficients.

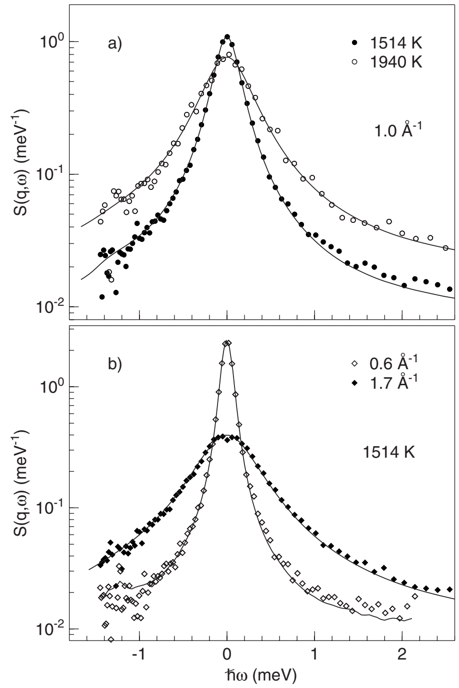

FIG. 1. Scattering law $S(q,\omega)$ of liquid Ni: (a) at fixed momentum transfer q for two different temperatures; more than 200 K above melting point (open circles) and more than 200 K below melting point (full circles), (b) at 1514 K (undercooled) for two q values, 0.6 and 1.7 $Å^{-1}$, respectively. The lines are fits with a Lorentz function that has been convoluted by the instrumental energy resolution function.

While the QNS measurements in the crucible were performed in a narrow regime of temperatures above the melting point, the application of the electromagnetic levitation technique gave access to a significantly wider temperature range, including also the metastable regime of an undercooled liquid. Over this large temperature range—from more than 200 K above to more than 200 K below the melting point of 1726 K—the temperature dependence of the diffusion coefficients can be described by an Arrhenius law,

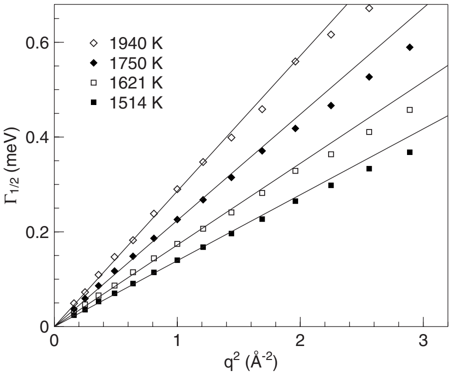

FIG. 2. q dependent linewidth of the scattering function $S(q,\omega)$ for different temperatures. Lines are fits with Eq. (2) in the q range of 0.6–1.5 $Å^{-1}$.

TABLE I. Ni self-diffusion coefficients determined by quasielastic neutron scattering [$T_m(\mathrm{Ni})=1726$ K].

T (K)	D (10^{-9} m^2 s^{-1}) crucible[a]	D (10^{-9} m^2 s^{-1})[b]
1514 ± 5		2.09 ± 0.08
1621 ± 5		2.68 ± 0.12
1735 ± 5	3.27 ± 0.04	
1750 ± 5		3.47 ± 0.06
1795 ± 5	3.80 ± 0.06	
1810 ± 5		3.68 ± 0.07
1870 ± 5		4.05 ± 0.20
1940 ± 5		4.54 ± 0.23

[a] Reference 14.

[b] This work.

$$D = D_0 \exp(-E_A/k_B T), \qquad (3)$$

with an activation energy $E_A=470 \pm 30$ meV/at. and a prefactor $D_0=(77 \pm 8) \times 10^{-9}$ m^2 s^{-1}. This also shows that the change from a liquid in thermodynamical equilibrium to a metastable liquid at temperatures below the melting point is not reflected in its atomic dynamics.

The Arrhenius behavior observed here for liquid Ni differs from the T^2 behavior reported for metallic melts with lower density of packing such as Sn, Pb, In, and Sb.[25,26] There, long-capillary experiments were performed in space under microgravity conditions, where the absence of buoyancy-driven convective flow resulted in the required precision of the diffusion coefficients. As shown in Fig. 3 the Ni data cannot be described with $D(T) \propto T^2$. As a consequence, a T^2 behavior of the temperature dependence of the self-diffusion coefficient does not hold as a general rule in one-component liquid metals around the melting point.

In dense packed liquids mode-coupling theory predicts a temperature dependence of diffusion of $(T-T_c)^\gamma$ close to a critical temperature T_c.[27] We were not able to undercool liquid Ni to temperatures where such a behavior is expected. However, the addition of P, Pd, and Cu to Ni significantly reduces the liquidus temperature of the system. Around the liquidus temperature of 865 K, in the $\mathrm{Pd_{43}Ni_{10}Cu_{27}P_{20}}$ alloy atomic dynamics are in accordance with the mode-coupling theory of the liquid to glass transition and Ni self-diffusion coefficients are proportional to $(T-T_c)^\gamma$, with $\gamma=2.7$ and $T_c=710$ K.[6] At higher temperatures the Ni self-diffusion coefficient of the Pd-Ni-Cu-P alloy[14] becomes as large as the measured diffusion coefficient for pure liquid Ni and exhibits also a temperature dependence that is well described with an Arrhenius law.

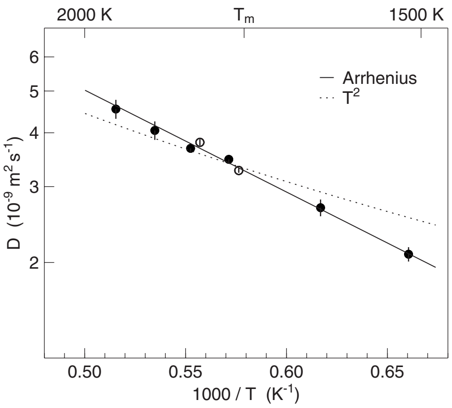

FIG. 3. Ni self-diffusion coefficients D as a function of inverse temperature in a range spreading from more than 200 K above to more than 200 K below the melting point. The full circles are the data points determined by the levitation experiments of this work, and the open circles are data points from the experiments of Ref. 14. The line is an Arrhenius fit of the experimental data resulting in an activation energy of 0.47 eV/at.. The dashed line represents the best fit with a T^2 law.

To summarize, we present an experimental technique to measure self-diffusion coefficients in liquid metals in a broad temperature regime that are not hampered by convection. The combination of the containerless processing technique of electromagnetic levitation with quasielastic neutron scattering allows us to determine self-diffusion coefficients with high precision even for chemically reactive melts. Moreover, by avoidance of heterogeneous nucleation at crucible walls, the melts can be undercooled below the equilibrium melting temperature such that diffusion data are available also in the metastable regime of an undercooled liquid. The developed technique will enable systematic studies of the diffusion processes in metallic alloy melts and will provide the experimental basis to obtain a profound physical understanding of diffusion in liquid metals and alloys. As a first application we have shown that the previously debated T^2 behavior of the temperature dependence of diffusion is not generally applicable for one-component metallic liquids and that the diffusive dynamics in liquid Ni in the equilibrium and in the metastable state does not differ on an atomic scale.

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