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Anomalously Fast Diffusion of Cobalt in β-Zirconium: Evidence for Two Different Jump Frequencies from Quasielastic Neutron Scattering

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Quasielastic line broadening of neutrons scattered from β-Zr alloyed with 2 at.% Co indicates that all Co atoms, not merely a small fraction, participate in fast diffusion. At 1100 °C the deduced Co jump frequency is about 25 times higher than that of the Zr atoms but about 6 times lower than the Co jump frequency deduced from tracer measurements. This discrepancy and an anomalous decrease in scattering intensity above 1100 °C indicate that a second Co jump frequency exists which is several hundred times higher than that of the Zr atoms.

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We report on a direct measurement of a jump frequency for anomalously fast diffusion of solute atoms in a metal. In some elements, particularly lead, tin, and the IV*b* metals titanium, zirconium, hafnium, a number of solute atoms diffuse orders of magnitude faster than the host atoms. This interesting phenomenon cannot be explained by the usual vacancy diffusion mechanism. An extreme interaction with vacancies or an interstitial mechanism must rather be invoked.[1-5] Details, however, are uncertain because the commonly used method, i.e., tracer diffusion technique, cannot study the diffusion jump in itself, but measures the total mass transport. Techniques which can directly study the atomic jumps are therefore highly desirable.

We carried out the first direct measurement of the jump frequency in an anomalously fast diffusion process by using incoherent quasielastic neutron scattering (QNS).[6,7] With QNS the Fourier transform of the self-correlation function of a jumping atom is determined. The quasielastic broadening of the scattered intensity yields the jump frequency; its dependence on the scattering vector when measured on a polycrystal yields the jump length.

For our studies we have chosen the anomalously fast diffusion of Co in β-Zr (the bcc high-temperature phase of Zr). This system has been studied earlier by the tracer technique.[8-10] For QNS studies Zr+2-at.% Co has two essential advantages compared to other alloys exhibiting anomalously fast diffusion:

(i) In the temperature region between 833 and 1400 °C the Co solubility limit is not exceeded.[11]

(ii) Co has a high cross section for incoherent neutron scattering (4.8 b)[12] and Zr has an extremely low one (0.04 ± 0.01 b).[13] Thus, the dominating fraction of incoherent neutron scattering at a Zr+2-at.% Co alloy will be due to the Co atoms. The coherent diffuse scattering cross section or Laue cross section per Co atom of this alloy is 2.5 b. In the case of a dilute and noninteracting alloy the quasielastic broadening of this coherent Laue scattering behaves like the incoherent scattering,[14] i.e., it is also described by the Fourier transform of the self-correlation function of the solute.

Items (i) and (ii) together imply that Zr+2-at.% Co is incomparably better suited for QNS studies than one of the well-known fast-diffusing Pb systems, where the solubility of the fast diffuser (Cu, Au, etc.) is only of the order of 10 to 1000 ppm. Hence the incoherent scattering intensity is orders of magnitude higher for Co in β-Zr than for any Pb system.

Polycrystalline alloy samples were produced by levitation melting of high-purity Zr [received from (a) MSG company, (b) Chalk River Nuclear Laboratories, or (c) MRC] and Co in inert gas atmosphere. Great care was taken to keep the content of gaseous impurities as low as possible. Analyses performed by way of hot extraction gave the following contents of oxygen/nitrogen (in atomic parts per million) in the alloys: (a) 220/20, (b) 660/4000, and (c) 5500/(not determined). The hydrogen content was in all cases below the detection threshold of the analysis (500 at. ppm). The QNS measurements discussed below showed no systematic difference between the results obtained with the three types of material.

Measurements at eight different temperatures were performed with the backscattering spectrometer IN10 at the high-flux reactor of the Institut Laue-Langevin. The incident energy was 2 meV, the energy resolution 1 μeV (full width at half maximum). No Bragg peaks occurred in the Q range from 0.6 to 1.9 Å^{-1} investigated. The results were treated in the usual way: After subtraction of the empty-can data the spectra were normalized with a calibration run performed with a vanadium standard. Cylinder corrections were applied to eliminate the influence of self-shielding and absorption.

Figure 1 shows energy spectra of neutrons scattered at Zr+2-at.% Co at three different temperatures. In the spectra the normalized intensity $S(Q,\omega)$ is plotted versus the energy transfer of the scattered neutrons. A quasielastic broadening is observed which increases with temperature. The curves in Fig. 1 were obtained in the following way: The spectra were fitted with a scattering law consisting of a sum of a delta function and a Lorentzian both convoluted with the experimentally determined resolution function. The essential fit parameters were the weights of the elastic and quasielastic components and the width $\Delta\Gamma$ (full width at half maximum) of the Lorentzian. The elastic intensity agrees well with the intensity obtained from a measurement of neutrons scattered incoherently from the Zr reference sample, both measured at the same temperature. This intensity is therefore attributed to the incoherent scattering at the Zr atoms in accordance with the fact that the Zr diffusivity is too low to be resolved by the spectrometer over almost the entire temperature range studied in this work.[15] After it had been proved that the elastic intensity was attributable to scattering from the Zr atoms its fraction was kept fixed at the average value of 0.27. This resulted in a considerably more reproducible fitting of the broadening of the quasielastic component.

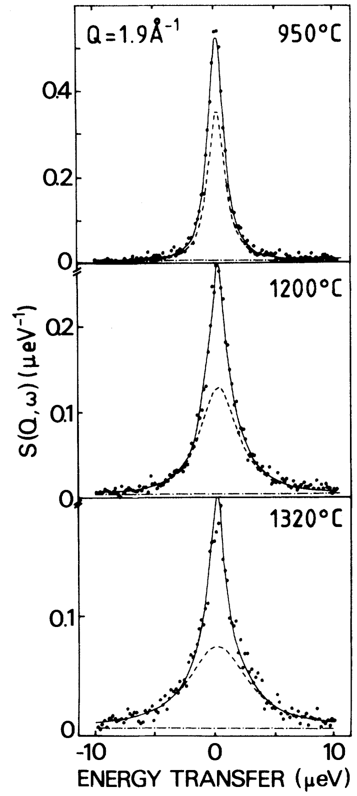

FIG. 1. Normalized intensity $S(Q,\omega)$ of neutrons scattered at Zr+2-at.% Co at different temperatures for a momentum transfer $Q = 1.9$ Å^{-1}. The dashed curve represents the quasielastic intensity, the continuous curve the sum of the elastic and quasielastic intensity with fixed fractions of 0.27 and 0.73, respectively.

The fact that there is no elastic intensity beyond that attributable to scattering at Zr atoms indicates that in β-Zr+2-at.% Co practically *all* Co atoms participate in diffusion jumps which are much more frequent than those of the Zr atoms. This result is somewhat surprising, since it means that approximately 2% of all atoms (the Co atoms) are moving rapidly through the relatively immobile lattice of Zr atoms, i.e., a situation which is comparable to the diffusivities of gaseous impurities in metals even though the Co diffusivity is still much smaller. This demonstrates that at least for the system Co in β-Zr *we have to reject any model where only a small fraction of all atoms participates in fast diffusion.*

The width of the quasielastic Lorentzian increases rapidly with increasing temperature and depends on the momentum transfer Q. This is shown in Fig. 2

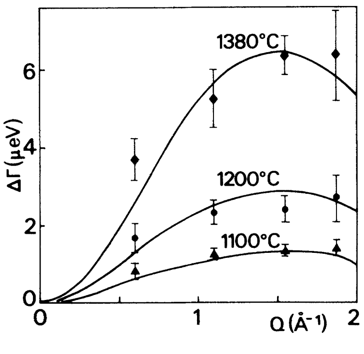

FIG. 2. Quasielastic broadening $\Delta\Gamma$ measured as a function of Q for various temperatures. The curves represent solutions of Eq. (1) with the nearest-neighbor jump distance $l = 3.1$ Å.

where the quasielastic broadening $\Delta\Gamma$ is plotted as a function of Q for various temperatures. Fitting the Q dependence of $\Delta\Gamma$ with the expression

$$\Delta\Gamma = (2\hbar/\tau)[1-(\sin Ql)/Ql]f, \qquad (1)$$

which is a reasonable approximation for a polycrystalline sample,[16] we can determine the length l of an elementary diffusion jump. $1/\tau$ is the jump frequency and f the correlation factor which corrects for the fact that the directions of successive jumps may be correlated with one another. A best fit gives $l = 3.0 \pm 0.3$ Å, a figure which is comparable to the nearest-neighbor distance 3.1 Å in the Zr lattice. Figure 3 shows the broadening of the quasielastic line at high Q as a function of the reciprocal temperature. Together, the results presented in Figs. 2 and 3 permit a determination of $(1/\tau)f$ in the temperature range between 950 and 1380 °C.

From the Einstein-Smoluchowski relation $D = l^2 f/6\tau$ we can now calculate the diffusivities D, assuming a jump length $l = 3.1$ Å and further assuming that the same correlation factor enters into the quasielastic line broadening and the diffusivity. We find that the diffusivities calculated in this way are considerably lower than those determined from tracer experiments on the same alloy, Zr + 2-at.% Co.[8] For example, at 1100 °C we obtain $D = (1.6 \pm 0.3) \times 10^{-7}$ cm^2/s; although this is still about 25 times larger than the tracer diffusivity for Zr diffusion, it is about one-sixth of that measured for Co diffusion, both values referred to 1100 °C. The same relations hold for the jump frequencies.

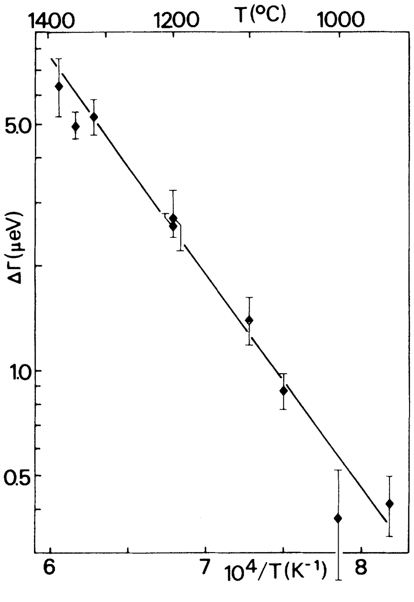

FIG. 3. Quasielastic broadening $\Delta\Gamma$ measured as a function of temperature for $Q = 1.9$ Å^{-1}. The straight line represents an Arrhenius fit with $\Delta\Gamma = 3.3 \times 10^4 \times \exp[-(1.20\ \mathrm{eV})/k_BT)]$ μeV.

This discrepancy is puzzling, and might lead to speculation on the difference between information obtained by microscopic methods such as QNS and by macroscopic methods such as tracer diffusion. We suspected the following solution: A fraction of the Co atoms might diffuse much faster than the rest (already fast moving compared with the Zr atoms) and give rise to an unresolved very broad quasielastic line.

Measurements were performed with the aim of searching for very broad quasielastic line. Strong though indirect evidence for the existence of such a component was found by studying the temperature dependence of the total scattered intensity. Figure 4 shows that above 1100 °C the measured total scattered intensity decays much faster than would be expected from a Debye-Waller-factor-like high-temperature approximation $I \propto \exp(-3\hbar^2 Q^2 T/k_B\theta_D^2 m)$. Here θ_D is the Debye temperature, m is the mass of the scattering atom, and the other symbols have their usual meanings. (The Debye temperature was estimated from lattice-dynamics measurements[17] of β-Zr: $\theta_D = 220$ K.) The anomalous decrease in intensity above 1100 °C gives evidence of an undetected very broad quasielastic component, which at lower temperatures is partly hidden in the shoulders of the spectra and above 1100 °C disappears in the background, thus simulating a decrease in intensity. An estimate from the anomalous decay in intensity shows that this component should be connected with about 25% of the scattering at the Co atoms and with a jump frequen-

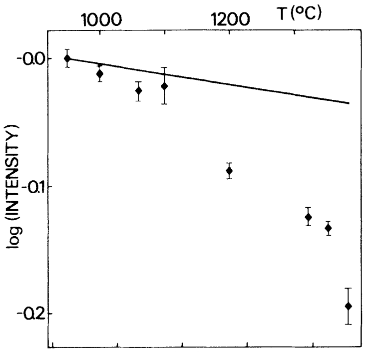

FIG. 4. Normalized total intensity I of neutrons scattered at Zr + 2-at.% Co as a function of temperature for $Q = 1.9$ Å^{-1}. The straight line represents the expected Debye-type behavior of the scattered intensity with $\theta_D = 220$ K, normalized to the measurement at 950 °C.

cy several hundred times higher than that of the Zr atoms.

Here we refrain from guessing whether jumps between interstitial sites might be the reason for the fast diffusion of Co. We expect more information, particularly on the jump vector of the slower jump, from measurements on single crystals which we hope to grow.

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