

EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Proposal to the ISOLDE and Neutron Time-of-Flight Committee

Tracer diffusion and PAC measurements of $^{111\text{m}}\text{Cd}$ tracer atoms in A_3B compounds

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Abstract

We propose to perform concerted measurements of long-range tracer diffusion of $^{111\text{m}}\text{Cd}$ isotopes in A_3B compounds (A= In, Sn, Ga, Al and B= rare-earth) and the corresponding jump frequencies of these atoms in the same compounds using radiotracer and perturbed angular correlation (PAC) methods, respectively, at ISOLDE-CERN. The combination of diffusivity and jump-frequency data will allow to determine the correlation factor for vacancy-mediated diffusion. For the first time, a direct approach to experimental measurements of the correlation factor will be followed using state-of-the-art facilities.

Requested shifts: 20 shifts, (split into 3-4 runs over 2 years)

Introduction



Diffusion, or atom movement, in metallic solids generally occurs via a vacancy mechanism, in which atoms are only able to move by jumping into neighboring vacant lattice sites. Atom transport can be expressed quantitatively in terms of either the diffusivity D or mean jump-rate ω . An atom that exchanges place with a vacancy has a greater than average probability to make a subsequent jump backward in the direction of the vacancy. This correlated motion reduces the effectiveness of jumps for atom transport. For a cubic solid, D and ω are connected via the general relation $D = f l^2 \omega / 6$, in which l is the jump-distance and f is the correlation factor that is of central interest to this proposal. For a truly random walk, $f = 1$, and departure of f from unity (typically smaller than unity) reflects non-randomness in the jumps [Ph91]. Being just the given number (e.g. $f = 0.7815$ for FCC lattice) for *self-diffusion*, the correlation factor becomes a function of different jump rates for *solute* diffusion and thus temperature-dependent [A193,Ph91]. Imagine that a solute atom is tightly bound to a vacancy. Loosely speaking, the solute's motion will then depend on the ratio of the jump-rate for exchange between solute and vacancy, ω_2 , to the rate at which the vacancy can jump to equivalent, reoriented positions around the solute, ω_1 , see Fig. 1, which sketches vacancy (open square) jumps around a given solute (marked by "O" and positioned on the A sublattice in the L1₂-ordered A₃B lattice). When $\omega_1 \gg \omega_2$, memory of the preceding exchange gets lost, $f \approx 1$, whereas when $\omega_1 \ll \omega_2$, the solute mostly rattles back and forth between two sites, without effective mass transport ($f \approx 0$). Thus, the knowledge of the correlation factor is imperative for prediction of long-range diffusion based on known (e.g. calculated ab initio) jump barriers, since it provides the crucial insight into diffusion mechanism.

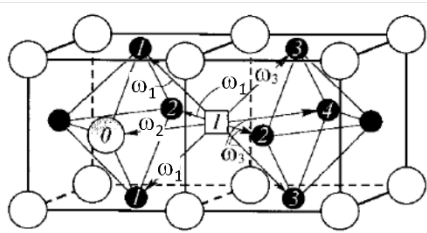


Figure 1: The ordered L1₂ structure A₃B, with A atoms (small filled circles) occupying face-centered sites and B atoms (large unfilled circles) the corner positions. Phases having this structure include, e.g., Ni₃Al and In₃Gd. The sublattice of A-atoms (lines connecting filled circles) is the relevant diffusion sublattice for which the correlation factor will be determined. The solute-vacancy exchange frequency is ω_2 and the ω_4 frequency (not shown) corresponds to a jump which is just the reverse of a ω_3 jump. ω_0 is the frequency of all jumps of the Ni vacancy more distant from the solute on the Ni sublattice [Di98].

More precisely, the correlation factor f is expressed as $f = u / (2\omega_2 + u)$, where u is the function of the frequencies indicated in Fig. 1 and can be found in terms of the five-frequency model [Ph91].

The correlation factor for self-diffusion (for which $\omega_2 = \omega_1$) is a constant that is straightforward to calculate and is basically a consequence of the connectivity of the lattice [M07], and D and ω are proportional at all temperatures. For an impurity, however, interaction with the vacancy will modify the local vacancy concentration as well as enthalpies for jumps of the vacancy close to the solute, including ω_1 and ω_2 . As a consequence, activation enthalpies for the diffusivity D and mean jump-rate ω of an impurity will in general differ from each other as well as from those of a host atom. The correlation factor for impurity diffusion (or solute diffusion) is expected to be strongly temperature dependent even for pure metals [M07] and the situation is even more complicated for diffusion in ordered alloys [Pa14].

Recently, Perturbed Angular Correlation of gamma rays (PAC), has been applied to measure diffusional jump-rates of probe atoms. The jumps produce fluctuating electric field gradients that cause relaxation of the nuclear quadrupole interaction. The measured relaxation can be

analyzed to obtain the mean jump rate using a stochastic atomic jump model [Za04]. PAC makes use of correlations between successive nuclear emissions to obtain a time-domain perturbation function that reflects precessions of nuclear moments in internal fields in solids (for an overview of PAC, see [Sc10]). While PAC is less well-known than other nuclear hyperfine methods such as Mössbauer effect and nuclear resonance, measurements can be made without any restriction in temperature, making it ideal for the study of diffusion at high temperature. As illustrated below, diffusional relaxation is exhibited as “damping” of the quadrupole perturbation function that can be fitted to obtain the mean jump frequency of the tracer probe atom. Using measurements of the diffusion coefficient D and jump-rate ω made for the same tracer element, f can be determined. The goal of this proposal is to carry out such a determination of f using and to demonstrate the feasibility of this approach for a set of carefully selected test systems.

PAC measurements of ω have been made at WSU for ^{111}In (^{111}Cd) tracer probe-atoms in many model phases A_3B having the ordered $L1_2$, or Cu_3Au , crystal structure shown in Fig. 1, with $A = \text{In, Sn, Ga, Al}$ and $B = \text{rare-earth}$ (see, e.g. [Co09, Co05, Ji09]). However, there exist no corresponding diffusion measurements for those systems and no PAC measurements using the $^{111\text{m}}\text{Cd}$ probe. Unfortunately, only few radioactive nuclei have all the favorable decay properties needed for PAC measurements and, in fact, all jump-frequency measurements to date have been made using ^{111}In parent probes, that decay by electron capture into an excited state of ^{111}Cd for which jumps are detected. Therefore, studies using the isomeric ^{111}Cd probe are required in order to eliminate any influence caused by after effects of nuclear decay following electron-capture in ^{111}In .

The probe atoms have to jump on a sublattice with lower than cubic symmetry so that the electric-field gradient changes in each jump; in this case the atomic jumps (exchanges with neighboring vacancies) could be followed by PAC and these jumps are simultaneously responsible for long-range diffusion.

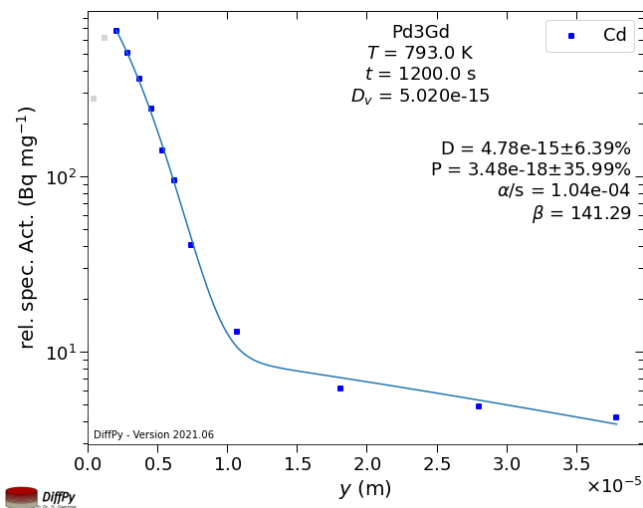


Figure 2. The penetration profile for $^{111\text{m}}\text{Cd}$ diffusion in Pd_3Gd at 793 K . The measured relative specific radioactivity was corrected for the short life time of the isotope. Two contributions, namely bulk and grain boundary ones, could be distinguished. The measurements were performed using On-Line Diffusion Chamber at ISOLDE.

On the other hand, the alloys have to be suitable for long-range tracer diffusion measurements, essentially pore-free and manufactured with macroscopic dimensions (preferentially discs of more than 5 mm in diameter and 1 mm thick). The $^{111\text{m}}\text{Cd}$ isotope has a short life time, about 48 min , however its diffusion can conveniently be measured using the On-Line Diffusion Chamber at ISOLDE. In Fig. 2, a penetration profile of $^{111\text{m}}\text{Cd}$ diffusion in Pd_3Gd is shown as an example. Thus, one could reliably determine the long-range tracer diffusion coefficients

of short-living $^{111\text{m}}\text{Cd}$ isotopes and, being combined with the jump frequency estimates from the PAC experiments (using the same isotope and the same sample material), will provide a direct access to the correlation factors of solute diffusion.

The $L1_2$ -ordered A_3B alloys provide a suitable class of systems for such direct measurements of the correlation factor via simultaneous application of the two complementary techniques if diffusion of the probe atoms will be limited to the A sublattice, see Fig. 1. Note that the radiotracer method is sensitive to tracer movement over macroscopic distances of about micrometer (from 100 nm to 1 mm, in fact), while PAC approach probes single jumps of the selected isotopes.

The correlation factor of tracer diffusion, although a fundamental quantity for defect-mediated diffusion, has never been measured for any system irrespective of more than 100 years of intensive research! The so-called isotope effect, being thought as a “holly grail” for the measurements of the correlation factor, provides lower limit of the corresponding value, due to unknown value of the kinetic energy transfer factor related to the by-passing the saddle-point configuration [M07]. The present proposal, if it will be granted, will for the first time provide a path for the direct measurements of the correlation factors in solid state diffusion.

Selected materials

The correlation factor for Cd solute diffusion in In_3Gd alloys will be determined by combining independent jump-frequency and tracer-diffusion coefficient measurements. In_3Gd is taken as a representative benchmark system, since Cd represents an In substitute and is likely to reside on the majority In sublattice in the $L1_2$ structure. The vacancy-mediated jumps of Cd atoms within the In sublattice could be probed by PAC and simultaneously they contribute to the long-range diffusion transport of the Cd isotopes (will be measured by the tracer technique using the existing On-Line Diffusion Chamber at ISOLDE).

All alloys have a finite compositional range between their boundary compositions. The influence of alloy composition on the correlation factor will be investigated through measurements on In_3Gd samples having the opposing phase boundary compositions, more In-rich and In-poor. This is because diffusion is governed by the concentrations of point defects--especially vacancies--which vary as a function of composition. It is of fundamental importance to elucidate how the correlation factor changes with composition.

The correlation factor for Cd solute diffusion will be determined also for Pd_3Sm alloys as an alternative model system. Differences between In-based and Pd-based alloys may give insight into a broader range of behaviors.

The A_3B systems having the $L1_2$ structure were chosen for study for the following reasons:

- (i) a suitable PAC-isotope $^{111\text{m}}\text{Cd}$ can be purely produced at ISOLDE-CERN;
- (ii) the results can be complemented by preliminary available jump-frequency measurements performed with $^{111}\text{In}(^{111}\text{Cd})$;
- (iii) extensive PAC measurements have been made on the entire series of In_3Ln and Pd_3Ln phases (Ln= lanthanide), including at opposing phase boundary compositions, such as shown in Fig. 3;
- (iv) diffusion of ^{111}Cd can conveniently be measured using existing On-Line Diffusion Chamber facility at ISOLDE;
- (v) the alloys are available for the two complementary measurement set-ups.

As one can see from Fig. 3, the jump-frequency is highly sensitive to the composition, even though boundary compositions of the In_3La and Sn_3La phases differ by only of the order of 0.2-1.0 at.%. For In_3Gd , jump-frequencies differ by a factor of three at the opposing phase boundary compositions. The In-rich and In-poor compositions of the In_3Gd phase are chosen as the main model system for the present study because of the availability also of In- and Gd-tracers that will allow ancillary self-diffusion measurements to be carried out. It should also be noted that solute diffusion in the $L1_2$ -ordered A_3B phase In_3Gd has attracted enormous interest in past, although the correlation factor in solute diffusion remains unknown due to a number of alternative, potential diffusion mechanisms (e.g. sublattice or anti-structure bridge mechanisms [Pa14, Di98]) and thus probable occurrence of inter- and intra-sublattice jumps for solutes with different activation energies [Di98].

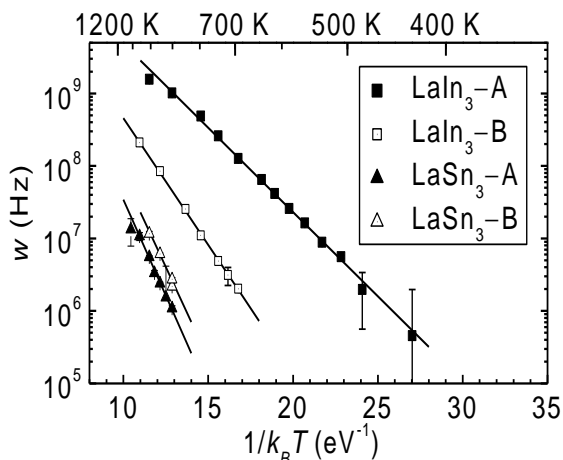


Figure 3. Arrhenius plots of jump frequencies obtained by fitting spectra such as shown in Fig. 4. From [Co05]. These are line compounds, with the two data sets coming from measurements for slightly different La-poor (A) and La-rich (B) boundary compositions.

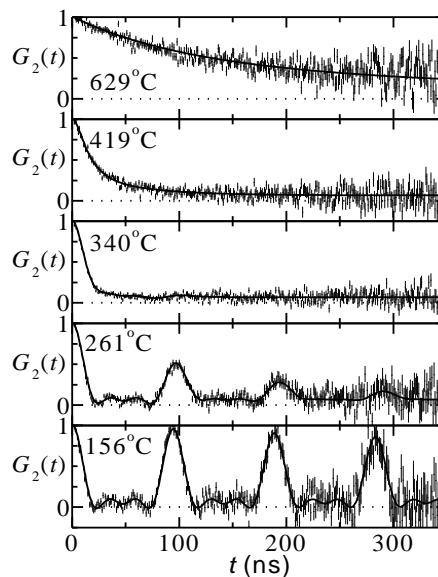


Figure 4. PAC perturbation functions for Cd probes on the In-sublattice in In_3La [Za04]. The damping is due to nuclear relaxation and can be fitted to obtain accurate values of the mean jump frequency over the entire range of temperatures.

The experimental measurements will be analyzed using the existing collaboration with well-known expert group of Dr. Tilmann Hickel with respect to DFT-based calculations of the correlation factors for Cd diffusion in the corresponding lattice as it was done recently [He21].

Summary of requested shifts:

Implanted beam	Probe element	Type of experiment	Approx. Intensity [at/ μ C]	Target / Ion source	Required atoms per sample	n° of shifts
^{111}mCd	^{111}mCd	PAC	10^9	Molten Sn/ VADIS	5×10^{10}	10
^{111}mCd	^{111}mCd	Diffusion	10^9	Molten Sn/ VADIS	5×10^{10}	10

References:

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Appendix

DESCRIPTION OF THE PROPOSED EXPERIMENT

The experimental setup comprises: *(name the fixed-ISOLDE installations, as well as flexible elements of the experiment)*

Part of the Choose an item.	Availability	Design and manufacturing
SSP-GLM chamber	<input checked="" type="checkbox"/> Existing	<input checked="" type="checkbox"/> To be used without any modification
Annealing furnaces 508-R-004	<input checked="" type="checkbox"/> Existing	<input checked="" type="checkbox"/> To be used without any modification <input type="checkbox"/> To be modified
	<input type="checkbox"/> New	<input type="checkbox"/> Standard equipment supplied by a manufacturer <input type="checkbox"/> CERN/collaboration responsible for the design and/or manufacturing
PAC spectrometers 508-R-008	<input checked="" type="checkbox"/> Existing	<input checked="" type="checkbox"/> To be used without any modification <input type="checkbox"/> To be modified
	<input type="checkbox"/> New	<input type="checkbox"/> Standard equipment supplied by a manufacturer <input type="checkbox"/> CERN/collaboration responsible for the design and/or manufacturing
[insert lines if needed]		

HAZARDS GENERATED BY THE EXPERIMENT

(if using fixed installation) Hazards named in the document relevant for the fixed [COLLAPS, CRIS, ISOLTRAP, MINIBALL + only CD, MINIBALL + T-REX, NICOLE, SSP-GLM chamber, SSP-GHM chamber, or WITCH] installation.

Additional hazards:

Hazards	[Part 1 of the experiment/equipment]	[Part 2 of the experiment/equipment]	[Part 3 of the experiment/equipment]
	Thermodynamic and fluidic		
Pressure	[pressure][Bar], [volume][l]		
Vacuum			
Temperature	[temperature] [K]		
Heat transfer			
Thermal properties of materials			
Cryogenic fluid	[fluid], [pressure][Bar], [volume][l]		
Electrical and electromagnetic			
Electricity	[voltage] [V], [current][A]		
Static electricity			
Magnetic field	[magnetic field] [T]		
Batteries	<input type="checkbox"/>		
Capacitors	<input type="checkbox"/>		
Ionizing radiation			
Target material	[material]		

Beam particle type (e, p, ions, etc)	^{111m} Cd ions		
Beam intensity	10 ⁹ at/ μC of ^{111m} Cd (standard)		
Beam energy	30 to 50 kV		
Cooling liquids	[liquid]		
Gases	[Argon]		
Calibration sources:	<input type="checkbox"/>		
• Open source	<input type="checkbox"/>		
• Sealed source	<input type="checkbox"/> [ISO standard]		
• Isotope			
• Activity			
Use of activated material:			
• Description	<input type="checkbox"/>		
• Dose rate on contact and in 10 cm distance	[35][uSV]- [10][uSV]		
• Isotope	^{111m} Cd		
• Activity	5 x 10 ¹⁰ atoms per sample		
Non-ionizing radiation			
Laser			
UV light			
Microwaves (300MHz-30 GHz)			
Radiofrequency (1-300MHz)			
Chemical			
Toxic	[chemical agent], [quantity]		
Harmful	[chemical agent], [quantity]		
CMR (carcinogens, mutagens and substances toxic to reproduction)	[chemical agent], [quantity]		
Corrosive	[chemical agent], [quantity]		
Irritant	[chemical agent], [quantity]		
Flammable	[chemical agent], [quantity]		
Oxidizing	[chemical agent], [quantity]		
Explosiveness	[chemical agent], [quantity]		
Asphyxiant	[chemical agent], [quantity]		
Dangerous for the environment	[chemical agent], [quantity]		
Mechanical			
Physical impact or mechanical energy (moving parts)	[location]		
Mechanical properties (Sharp, rough, slippery)	[location]		
Vibration	[location]		
Vehicles and Means of Transport	[location]		
Noise			
Frequency	[frequency],[Hz]		
Intensity			
Physical			
Confined spaces	[location]		
High workplaces	[location]		
Access to high workplaces	[location]		
Obstructions in passageways	[location]		

Manual handling	[location]		
Poor ergonomics	[location]		

0.1 Hazard identification

3.2 Average electrical power requirements (excluding fixed ISOLDE-installation mentioned above): *(make a rough estimate of the total power consumption of the additional equipment used in the experiment)*