Studies of atomic diffusion in Ni–Pt solid solution by x-ray photon correlation spectroscopy

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Abstract

Atomic scale x-ray photon correlation spectroscopy (aXPCS) was used to study atomic diffusion in the Ni\textsubscript{97}Pt\textsubscript{3} solid solution with both a single crystal and a polycrystalline sample. Different jump diffusion models are discussed using experimental results and Monte Carlo simulations. The sensitivity of aXPCS experiments to short-range order (in this case governed by a strong Pt–Pt repulsive force) is demonstrated. The activation energy of 2.93(10) eV as well as diffusivities in the range of \(10^{-23}\) m\(^2\) s\(^{-1}\) at 830 K agree very well with the results of tracer diffusion studies at much higher temperatures.

(Some figures may appear in colour only in the online journal)

1. Introduction

A variety of well established methods can be applied to investigate diffusion in solid state systems [1]. However, studies of diffusion mechanisms on the atomic scale are still challenging. Atomic scale x-ray photon correlation spectroscopy (aXPCS) can provide new insight into this field.

XPCS is the x-ray analogue of the very successful technique of dynamic light scattering also called photon correlation spectroscopy [2]. PCS is well established for characterizing the equilibrium dynamics of soft condensed matter by determining the intensity autocorrelation function of the scattered laser light as a function of delay time and wavevector transfer. Similarly, using coherent synchrotron radiation instead of visible laser light, XPCS [3] is being widely applied for studies of soft matter dynamics where objects are in the nanometre range (see e.g. [4–7]). Attention has also been directed towards metal systems with the feasibility test on the (100) Bragg peak of Cu\textsubscript{3}Au [8] and an investigation of critical dynamics in Fe\textsubscript{3}Al [9]. Because of the short x-ray wavelength, XPCS seems to be ideal for studies at atomic length scales. These types of experiments had, however, never been reported in the literature until a successful demonstration of the capability of XPCS to resolve single atomic motion in condensed matter [10]. Particularly, we have clarified the mechanism of atomic dynamics in Cu\textsubscript{90}Au\textsubscript{10} [10, 11] and studied dynamics in a metallic glass [12].

The goal of this paper is to describe in detail the atomic motion of dilute platinum atoms in a nickel matrix at relatively low temperatures. The Ni\textsubscript{97}Pt\textsubscript{3} intermetallic alloy is a perfect candidate for studying diffusion of small quantities of dilute atoms due to its outstanding intensity of diffuse scattering even for low solute concentration levels. Moreover, profound questions can be addressed regarding interactions between solute atoms and vacancies. It is well known that vacancies are vehicles of diffusion in alloys [1], but the interactions between the vacancy and solute atom can radically influence the motion of the latter. Our objective is to analyse these interactions with the help of aXPCS. These questions were addressed in the past by a number of methods such as Mössbauer...
spectroscopy, nuclear resonant scattering or quasi-elastic neutron scattering [13]. The elementary diffusion steps were investigated for self-diffusion [14], for impurity diffusion with consideration to the interaction with vacancies [15], for hydrogen in intermetallic hydrides [16] and in intermetallic B2 [17–19] and DO3 [20] phases. All methods mentioned above have in common that they are limited to only a few selected isotopes and have a poor energy resolution, which makes measurements at very high temperatures necessary (apart from hydrogen). The time-domain technique of aXPCS, on the other hand, is free from these restrictions.

The important aspect of this paper is studying diffusion in single crystal and polycrystalline samples of the same composition. For methods studying spatially resolved atomic motion such as aXPCS, single crystal samples provide the possibility to investigate different crystallographic directions and therefore obtain more information than polycrystalline samples. It is, however, sometimes difficult or even impossible to obtain single crystals of satisfactory quality. Showing that studies on polycrystals can, in whole or in part, provide information on a comparable level when using a coherent method, a new field of materials could be investigated with aXPCS. Ni$_2$Pt$_3$ seems to be an ideal object for such a study.

2. Theory

Nowadays, atomic structures can be investigated at their elemental scale. Still, monitoring a single atom in a bulk sample on timescales of atomic diffusion is not possible in real space. It is however possible to measure dynamics in a reciprocal space which corresponds to these dynamics in real space. Usually, reconstruction of real space from a scattering image is very challenging due to the phase problem. Fortunately, one can ignore the details of the exact structure image is very challenging due to the phase problem.

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The autocorrelation function of the electric field $g(t) = \langle E(0) E(t) \rangle$ is connected by the Siegert relation for Gaussian scattering processes [21]. Therefore it is sufficient to measure the intensity autocorrelation function to gain information about the dynamics in real space

$$g(\vec{q}, \Delta t) = 1 + \beta \exp(-2\Delta t / \tau(\vec{q})).$$

The intensity autocorrelation function for perfectly coherent radiation would decline from a value of 2 to 1. However, because of an x-ray beam being only partially coherent in the experimental setup the coherence factor $\beta$ [24] is diminished. The correlation time $\tau(\vec{q})$ is given by

$$\tau(\vec{q}) = \frac{I_{SRO}(\vec{q})}{\sum_n P_n \sum_{\Delta \vec{a}_n} \left(1 - \exp(i \cdot \Delta \vec{a}_n)\right)}.$$  

This follows from the theory describing the short-range order and coherent dynamics in a linear approximation as derived by Sinha and Ross [25]. It is discussed in more detail in Leitner and Vogl [11]. $\tau_0$ is the average time between jumps of an atom and therefore corresponds to the inverse of the average jump frequency $\nu_0^{-1}$. The probability for an atom to jump to one of the lattice sites of a certain neighbouring shell is given by $P_n$, with $n$ being the number of the appropriate coordinate shell (1 for nearest-neighbour, 2 for next-nearest-neighbour and so on). The vector $\vec{a}_n$ points from the origin to the $n$th site in the $n$th shell. It can be easily seen that the inverse correlation time is the sum over the inverse correlation times for each shell corresponding to the particular jump mechanism [13]. Therefore it can also be written as $\tau(\vec{q})^{-1} = \sum_n \tau_n(\vec{q})^{-1}$.

In a polycrystalline sample, one has to average over all orientations of $\vec{q}$ with respect to the crystal lattice

$$g(\vec{q}, \Delta t) = 1 + \frac{\beta}{4\pi} \int_{\vec{q} = \vec{q}} d\vec{q} \cdot \exp(-2\Delta t / \tau(\vec{q})).$$

It is essential for the method at hand to be able to fit the data set with a function depending on $\Delta t$. As there is no analytical function which satisfies equation (4), an approximation has to be made. A similar approach was introduced by Chudley and Elliott [26] for liquids. Exchanging integration and exponentiation, an average correlation time $\tau(\vec{q})$ can be defined as $\tau(\vec{q})^{-1} := (4\pi)^{-1} \int_{\vec{q} = \vec{q}} d\vec{q} \cdot \tau(\vec{q})^{-1}$. For this expression an analytical
Nickel and platinum, both of 99% purity, were melted by induction heating in a ‘cold boat’ in argon atmosphere. For the preparation of the polycrystalline sample the resulting ingot was cut and rolled between stainless steel plates down to a thickness of 17 µm. It was then pre-annealed at a temperature of 773 K for 22 h in a vacuum of about 10⁻⁶ mbar. In order to obtain sufficiently large single crystalline domains the rest of the ingot was heat treated at 1573 K for 140 h, resulting in crystallites of about 5 mm diameter. One domain was oriented, cut with a wire saw and mechanically polished to the final thickness of about 18 µm. The composition of the sample was analysed by energy-dispersive x-ray spectroscopy (EDX), showing 3.0(5) at.% platinum content.

The experiment was performed at beamline ID10A of the ESRF using a standard coherent setup with 8 keV photons at a monochromaticity of ΔE/E ≈ 10⁻⁴. Rollerblade slits were used to select an 8 × 8 µm² beam section and speckle patterns were recorded with a direct-illumination CCD camera with 1024 pixels × 1024 pixels at a size of 13 × 13 µm². Prior experience has shown that the CCD camera placed close to the sample (about 0.6 m) is advantageous to maximize the measured signal. It was mounted in a way that allowed its movement through a scattering angle 2θ and an azimuthal angle φ. Note that in a scattering experiment the length of the scattering vector is connected to the scattering angle 2θ via $q = 2|k| \sin(2θ/2)$, with $k$ being the wavevector of the incoming beam. As one can move freely on the Ewald sphere in reciprocal space by changing the detector position in real space, the intensity autocorrelation function was measured for several $q(2θ, φ)$. In the polycrystalline sample only the scattering angle 2θ (i.e. $q̂$) can influence the correlation time. Therefore measurements at arbitrary azimuthal angles are equivalent. For the single crystal sample an additional second scan for fixed $q̂$ and different azimuthal angles $φ$ was performed. Measurements were performed in transmission geometry in a resistively heated vacuum furnace ($ρ ≤ 10⁻⁶$ mbar). The temperature was stabilized by a PID temperature controller within a range of 0.1 K. The measurement time at a fixed scattering vector $q̂$ was between 20 and 40 min at a frame rate of one frame every 10.9 s (exposure plus readout time). Due to the limited intensity of the synchrotron source and low scattering intensity at large scattering angles in the diffuse regime it is beneficial to make the data collected by the CCD camera subject to the so-called droplet algorithm [27] to detect single photon events. Our implementation of the droplet algorithm is described in [28]. The corrected images were evaluated according to equation (1), finding the correlations in the fluctuating speckle intensities (see figure 1), where the autocorrelation function was averaged over all pixels to obtain sufficient statistical accuracy.

All measurements were carried out in the diffuse regime, away from Bragg peaks. Any kind of strain broadening or asymmetry resulting from dislocations, planar faults etc are constrained to $q$-regions very close to the Bragg reflections [29]. Therefore such effects do not influence the intensities obtained in an aXPCS experiment. The number of vacancies relative to the number of atoms in Ni at 830 K is in the order of 10⁻⁸ [30]. Therefore the total scattering power of the vacancies and their induced displacements is negligible. A further contribution originating from thermal diffuse scattering can be estimated to be on the order of 10⁻³, using the Debye model at this temperature. This contribution can therefore also be neglected. As a result the diffuse intensity is only due to the stochastic occupations of lattice sites by Ni or Pt, and the measured correlation decay therefore corresponds to exchanges of atoms.

In the case of diffusive dynamics, small absolute values of reciprocal vectors correspond to very long correlation times. Instabilities of the experimental setup result in additional intensity variations. This can lead to faults when overlapping with the slowly decaying autocorrelation function caused by the sample itself, but is not important if the timescale of both processes is clearly different. Correlation times measured at very small 2θ angles were therefore not used for the evaluation of diffusion models.

It is vitally important for aXPCS measurements to be performed in thermal equilibrium. To ensure that order
relaxation is negligible, multiple measurements were made repeatedly at different detector positions for each sample. Usually the sample relaxes faster when starting from a higher temperature and shows relaxation times of about 1 h. After that time the single crystal stayed stable during the whole experiment. The polycrystalline sample, however, seemingly relaxed again after about 4 h at 830 K, leading to still longer correlation times.

Note that the correlation time as measured in an aXPCS experiment quantifies the timescale over which the atomic arrangement changes by a sizeable amount. Even though effects such as enhanced grain boundary diffusion can affect the mass transport over macroscopic distances significantly, the contribution of the grain boundaries to the scattered signal and therefore to the correlation decay is negligible. As a consequence, aXPCS is inherently sensitive only to bulk diffusion.

To investigate whether there were crystallite growth effects in the polycrystalline sample during the experiment, the sample was studied with electron microscopy. Unfortunately the results were inconclusive. Therefore we assumed that such effects can be neglected as long as no relaxation in the correlation time is detectable.

4. Monte Carlo simulations

To simulate a simple diffusion model, Monte Carlo (MC) simulation of diffusion is a valuable approach. Two kinds of atom were arranged in a proportion of $N_{Pt}/N_{Ni} = 3/97$ over an fcc-type lattice with periodic boundary conditions. One vacancy was introduced by randomly emptying a lattice site. The simulation entails iteratively choosing one of the 12 lattice sites of the vacancy’s first coordination shell in a random fashion, then, according to the Metropolis algorithm, calculating the probability $p_{i \rightarrow f} = \exp(-\Delta E/k_B T)$. The energy difference $\Delta E = E_f - E_i$ is given by the system energies calculated with pair potentials for nearest-neighbours before (i) and after (f) the jump, respectively, $k_B$ is the Boltzmann constant and $T$ the absolute temperature. A decision to perform a jump or not was taken by comparing $p_{i \rightarrow f}$ with a random number. A unit time (MC step) was defined as the number of trials equal to the number of lattice sites. After equilibrating the system, the actual diffusion simulation was started. After each half Monte Carlo step a discrete Fourier transform of the lattice was carried out and the amplitudes were used to calculate the scattering intensity and the amplitude autocorrelation function $g^{(1)}(\mathbf{q}, t)$ for certain $\mathbf{q}$ values. Finally, using Siegert’s relation, the intensity autocorrelation function was calculated and compared with the experimental correlation time.

The same method was used to calculate short-range order intensities from a reciprocal space map of 64$^3$ voxels with an atom configuration of $4 \times 32^3$ atoms, averaging the intensities over 10 000 Fourier transforms.

5. Results

In order to distinguish between different diffusion models, measurements of intensity autocorrelation times in polycrys-

Figure 2. For a single crystal in the (110) orientation with azimuthal angle $\phi = 33.2^\circ$ the short-range order intensity was calculated without interaction between the atoms (red triangles) and for strong Pt–Pt repulsion (blue discs). For the latter the short-range order was also calculated from Warren–Cowley parameters obtained from the simulation (grey line). The inset shows the measured diffuse intensity as a function of the wavevector transfer.

talline and, respectively, in single crystal samples alone are insufficient. As shown in section 2 short-range order intensity plays a crucial role in the interpretation of the measured correlation times.

5.1. Short-range order

The particular importance of local atomic arrangements in alloys for the interpretation of aXPCS measurements follows from equation (3). Detailed data about SRO as in the case of Cu$_{90}$Au$_{10}$ [31] is rarely available. SRO must be actually measured for exactly the same alloy composition and temperature as the sample under study. It is very difficult to deduce short-range order data from experimentally measured intensity data. A detailed description of the diffuse scattering theory can be found in several articles and books (see e.g. [32, 33] and the literature cited therein). The factor which actually makes the analysis of diffuse scattering so difficult and time consuming is the separation of SRO scattering (which is of interest to us) and atomic displacement scattering. Simulations showed that in a system with a very high scattering contrast and low solute atom concentration such as Ni$_{97}$Pt$_3$, the magnitude of those two terms can be of the same order. Also terms of higher order in the expansion of diffuse intensity, e.g. caused by static displacements (Huang scattering) or thermal diffuse scattering, can play a role.

Phase diagrams of the Ni–Pt system [34] show three ordered equilibrium phases similar to Cu–Au: NiPt (L1$_0$ structure), Ni$_2$Pt, and NiPt$_3$ (both L1$_2$ structures). There was a weak tendency found for a Cu$_3$Au-type ordering for Ni$_{1-x}$Pt$_x$ with $x = 0.2$ composition [35] which is also indicated by the diffuse intensity for $x = 0.03$ as shown in the inset in figure 2. There is, however, no data for the short-range order configuration on a system with $x = 0.03$ available in the literature. Note that our main goal remains an atomistic diffusion mechanism and the details of the diffuse scattering intensity are not vitally important. Therefore we choose two simple models: (m1) a model with
no interaction between the atoms and (m2) a model with strong Pt–Pt repulsion force. The latter was chosen because an L1₂ ordering-type tendency resulting from strong Pt–Pt nearest-neighbour repulsion was assumed to be more likely than from Pt–Pt next-nearest-neighbour attraction or further ranging interactions. The two model systems m1 and m2 were simulated using a Metropolis Monte Carlo algorithm (see section 4). From the atomic configuration we calculated the Warren–Cowley parameters. In case of 3% solute atoms with strong repulsive force the calculated parameters were \( \alpha_1 = -0.0309 \), \( \alpha_2 = 0.0042 \) and \( \alpha_3 = 0.0018 \). These parameters can be used to calculate the short-range order intensity in Laue units according to

\[
I_{SRO}(\tilde{q}) = \sum_{n,j} \alpha_n \cos(\tilde{q} \cdot \Delta \tilde{a}_n),
\]

where \( \Delta \tilde{a}_n \) is again the family of vectors for a certain shell as discussed in section 2. As shown in figure 2 the so-calculated short-range order intensity is in good agreement with the intensities calculated directly from the Fourier transform of the real-space configuration.

5.2. Diffusion mechanism

The main objective of this paper is to discuss the mechanism which governs diffusion in a Ni–Pt intermetallic alloy. An essential advantage of a microscopic (atomistic) method in diffusion investigation is the possibility to identify such a diffusion mechanism. In order to verify which diffusion mechanism operates in a specific intermetallic phase, it is necessary to develop a mathematical model for the diffusion process. This mathematical idea is generated from the knowledge of the system or it is simply a right guess. The mathematical model can be (at least in certain cases) solved analytically and yields the wavevector dependent correlation time in a single crystal sample (see equation (3)), or the correlation time dependent on the magnitude of the wavevector in a polycrystalline sample (see equation (5)). A model is determined by the jump probability parameters \( P_n \).

The only free parameter fitted to the experimental data is the inverse average residence time \( \tau_0^{-1} \), which corresponds to the jump frequency.

Needless to say it is not particularly difficult to predict the atomistic mechanism of diffusion in Ni–Pt. It is simply an exchange of a nickel or platinum atom with a vacancy. As the scattering length of platinum considerably exceeds that of nickel and vacancies are very rare in the alloy at the temperatures of measurement, the detectable speckle fluctuations result predominantly from the exchanges of platinum atoms with nickel atoms. This very simple picture enables studies of further subtleties of the diffusion mechanism, such as the influence of interaction between solute atoms or between solute atoms and vacancies.

A simple and useful tool when discussing a diffusion model involving a vacancy is the so-called encounter approximation. It has been successfully applied in the interpretation of diffusion in nuclear magnetic resonance and in Mössbauer spectroscopy studies. An encounter is here defined as the sum of all exchanges of one and the same atom with one and the same vacancy. As the number of vacancies is much smaller than the number of atoms, the time between one and the same vacancy jumping twice is much smaller than the time between consecutive jumps of one and the same atom. Details during an encounter are thus ‘invisible’ for aXPCS and only a net result of one or more exchanges with a vacancy, which can carry an atom to nearest or to further neighbour shells, is accounted. Assuming that encounters are mutually independent one can therefore use a model of a simple random walk of the vacancy to calculate diffusivity.

In an fcc lattice the first neighbour shell is at a distance of \( a/\sqrt{2} \), the second of \( a \), the third of \( a\sqrt{3}/2 \) and fourth of \( a\sqrt{2} \), where \( a \) is the lattice constant. The nearest-neighbour shell can be reached by only one exchange between a solute atom and a vacancy. The second, third and fourth shells can, however, all be reached after two exchanges with a vacancy. Still farther shells (\( n \geq 5 \)) need three or more exchanges and can therefore be neglected. Also encounters that do not lead to an effective jump are invisible for an aXPCS experiment and are therefore neglected from here on (\( P_0 = 0 \)). We used this to re-normalize the jump probabilities for self-diffusion given in [38] and obtained jump probabilities of: \( P_1 = 92.6\% \), \( P_2 = 2.4\% \), \( P_3 = 3.9\% \) and \( P_4 = 0.8\% \) (the neglected probability for further jumps sums up to \( \sum_{n\geq5} P_n = 0.3\% \)). This encounter model (m1), however, describes only systems with negligible interactions between matrix atoms, solvent atoms and vacancies. Therefore we extend the encounter model according to equation (3), using the SRO intensity for strong Pt–Pt repulsion as discussed in section 5.1. We use this as a second model for the description of Pt diffusion and call it modified encounter model (m2).

In order to distinguish between the two models, correlation times were measured at a constant temperature of 830 K and at different detector positions corresponding to different \( \tilde{q} \) and [\( \tilde{q} \)] for the single crystal and the polycrystalline sample respectively.

MC simulations for different interaction energies between platinum atoms were carried out, one for no interaction between the atoms (s1), one with strong repulsive potential between Pt atoms (s2) and one with an attractive potential between Pt atoms (s3) within the first neighbour shell (\( n = 1 \)).

The experimentally measured data as well as the data from MC simulations and the models for a diffusion mechanism in the single crystal are shown in figure 3. Note that the only adjustment parameter is the jump frequency, which is simply a multiplicative constant. The figure shows that the MC simulation with no interaction potential (s1) complies with the encounter model for a system with no SRO (m1). The model with jump probabilities according to the encounter model and short-range order correction (m2) gives the same values as the simulated data for strong Pt–Pt repulsion (s2) and describes the experimental data sufficiently.
Reciprocal correlation times in a single crystal sample oriented in the (110) direction at 830 K. The (001) direction lies at $\phi = 0^\circ$. The radial scan (a) was taken at $2\theta = 23^\circ$. Both datasets were fitted simultaneously with the classical encounter model with no short-range order (m1) and with the modified encounter model with correction for the short-range order calculated for strong Pt–Pt repulsion (m2). For comparison, a model with only next-nearest-neighbour jumps (m3) can obviously be ruled out.

Figure 3. Reciprocal correlation times in a single crystal sample oriented in the (110) direction at 830 K. The (001) direction lies at $\phi = 0^\circ$. The radial scan (a) was taken at $2\theta = 23^\circ$. Both datasets were fitted simultaneously with the classical encounter model with no short-range order (m1) and with the modified encounter model with correction for the short-range order calculated for strong Pt–Pt repulsion (m2). For comparison, a model with only next-nearest-neighbour jumps (m3) can obviously be ruled out.

The polycrystalline sample was fitted by equation (6) and with the same jump probabilities as in the case of the single crystal. The short-range order correction was calculated by numerically integrating equation (7) over all orientations of $\vec{q}$. As mentioned in section 3, this sample was only quasi-stable for a limited time. It can therefore not be assumed that a sufficient number of small crystallites was covered by the beam during the measurement. For averaging over a small number of crystallites with unknown orientation the Chudley–Elliott model [26] is, however, still the best guess.

The calculated jump frequency using the modified encounter model as shown in figure 4 was $\tau_0^{-1} = 1.92(6) \times 10^{-3}$ s$^{-1}$. The difference from the single crystal value arises most likely from a difference in sample temperature, as a different furnace with a thermocouple at a different position with respect to the sample was used for this measurement. Again a model with only next-nearest-neighbour jumps (m3) can obviously not appropriately describe the measured data.

5.3. Activation energy and diffusion constant

The activation energy $E_A$ is the sum of a vacancy formation and migration energy. The relationship between diffusivity, temperature and activation energy can be described fairly accurately by the Arrhenius law [1]. A number of measurements were performed at different sample temperatures. Again measurements for different temperatures were repeated in order to guarantee thermal equilibrium of the sample.

Using the Einstein relation [40] and the sum of partial diffusion coefficients into farther shells one can write:

$$\tilde{D} = \frac{\langle R^2 \rangle}{6\tau_0} = \frac{1}{6\tau_0} \sum_n P_n |\Delta \vec{a}_n|^2,$$

where $|\Delta \vec{a}_n|$ is the radius of neighbour shell $n$. For fixed values of $\vec{q}$ one can use equation (3) to calculate the residence time $\tau_0$ from the measured correlation times $\tau(q)$ for each temperature. The lattice constant for Ni$_{97}$Pt$_3$ was calculated using Vegard’s law [41] and corrected for the thermal expansion at 830 K ($a = 3.545$ Å). With this value and using the modified encounter model the chemical diffusion coefficients $\tilde{D}$ can be calculated for each temperature, as shown in figure 5.

One should notice that a diffusion coefficient measured by the aXPCS technique is, owing to the coherency of the method, the chemical diffusion coefficient $\tilde{D}$. As already emphasized, exchanges between atoms of the same species do not influence the speckle pattern and are not recorded. However, in the case of our particular Ni–Pt solid-solution sample, chemical diffusion and self-diffusion coefficients of platinum are equal in a first approximation. This is simply a result of the low concentration of platinum atoms, which makes direct exchanges between them highly improbable.
interdiffusion \cite{39}, where the activation energy measured values are in excellent agreement with literature values for determining atomic jump vectors.

Diffusion rates measured by XPCS are on the order of and in very good agreement with the results of tracer methods. For measuring atomic diffusion process and the measured factors are reliable and the pre-exponential factor $D_0$ is $1.5(\pm4.6\times-1.1)\times10^{-5}$ m$^2$ s$^{-1}$ for the single crystal and $D_0$ for the polycrystalline sample, respectively, were very similar with $E_A$ for the polycrystalline sample, the blue line (solid) represents polycrystalline data and the red line (dash-dotted) represents the results of the tracer experiment.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{Chemical diffusion coefficients for polycrystalline (□) and single crystal sample (◇) compared to results from tracer measurements \cite{39} (○). The green line (dashed) represents the fit for the single crystal sample, the blue line (solid) represents polycrystalline data and the red line (dash-dotted) represents the results of the tracer experiment.}
\end{figure}

Using the Arrhenius law the activation energy as well as the pre-exponential factor $D_0$ can be calculated. Calculated activation energies for the single crystal and the polycrystalline sample, respectively, were very similar with $E_A$ for the single crystal and $E_A$ for the polycrystalline sample (Figure 5). The green line (dashed) represents the fit for the single crystal sample, the blue line (solid) represents polycrystalline data and the red line (dash-dotted) represents the results of the tracer experiment.

\begin{equation}
A\text{sc} = 9.39(\pm 9.39) \times 10^{-5} \text{ m}^2 \text{ s}^{-1} \text{ s}^{-1} \text{ m}^2 \text{ s}^{-1} \text{ m}^2 \text{ s}^{-1}
\end{equation}

$E_A$ for the single crystal and $E_A$ for the polycrystalline sample (Figure 5). The green line (dashed) represents the fit for the single crystal sample, the blue line (solid) represents polycrystalline data and the red line (dash-dotted) represents the results of the tracer experiment.

6. Conclusions

We could show that XPCS allows the observation of low concentrations of solute atoms if the electronic form-factor contrast between solvent and solute atoms is high enough. However, a higher brilliance of the coherent synchrotron radiation is crucial to be able to measure even more dilute samples. Correlated diffusion according to the encounter model with correction for short-range order effects is a simple atomic diffusion process and the measured factors are reliable and in very good agreement with the results of tracer methods. Diffusion rates measured by XPCS are on the order of $10^{-23}$ m$^2$ s$^{-1}$ and therefore on the lower border of what can be reached by the best tracer measurements. For measuring diffusivities this low, XPCS is the only method capable of determining atomic jump vectors.

The Pt–Pt repulsion indicated by the Monte Carlo simulation is in agreement with the Ni$_3$Pt phase \cite{34} for low platinum concentration. Although for an atomic concentration as small as 3% one cannot speak of a Ni$_3$Pt phase, the characteristic atomic interactions which lead to its formation are present. Due to insufficient accuracy it was, however, not yet possible to draw conclusions about solute–vacancy interaction from the comparison with simulations. With brighter synchrotron sources and better statistical significance coming along with them, it should be possible to investigate these features in the near future. Using Monte Carlo simulations on the basis of atomic interaction potentials and cluster expansion, aXPCS shows promise in being a valuable tool to confirm and test \textit{ab initio} calculated potentials.

X-ray photon correlation spectroscopy allows one to draw conclusions about the dominating diffusion mechanism. To distinguish subtle differences, e.g. whether the encounter model or a model with slightly different jump probabilities takes place, requires much better statistics than we could achieve in our experiment.

The experimental data from the polycrystalline sample showed generally good agreement in activation energy and diffusion rates with the tracer method. It seems also possible to reveal the dominating diffusion mechanism (in this case nearest-neighbour jumps) with these data. In order to prepare polycrystalline samples allowing for exact measurements of diffusion rates, efforts have to be made to prepare samples with sufficiently small crystallites and to eliminate crystal lattice growth effects. Especially, aXPCS experiments on powder samples seem to be particularly promising in this regard.

Overall we conclude that aXPCS is a very reliable method for investigating atomic diffusion for all types of alloys and provides a reasonable reference for \textit{ab initio} simulations.

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