

# Atomic Dynamics in Decagonal Al-Ni-Co Quasicrystals

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## Abstract

The atomic dynamics of decagonal Al-Ni-Co quasicrystals is investigated by molecular dynamics simulations. The model structures used consist of an alternating stacking of two layers, which are decorations of a hexagon-boat-star tiling. Apart from small relaxations, these model structures are essentially stable up to the melting point. Above two thirds of the melting temperature, a large fraction of the aluminium atoms becomes mobile, and long range atomic diffusion sets in, without destroying the overall structure. The diffusion of aluminium is analyzed as a function of temperature and pressure, and the microscopic diffusion processes are discussed.

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## 1. Introduction

Molecular dynamics (MD) is an excellent tool for the study of the microscopic processes of atomic dynamics. Due to the aperiodic nature of quasicrystals, any reasonable model structure requires so many atoms, that a quantum mechanical treatment of the interactions between the atoms is infeasible, so that classical, effective potentials have to be used. The quality of the results of MD simulations crucially depends on the quality of these potentials, and the construction of reliable potentials is a very difficult task.

MD simulations of decagonal Al-Cu-Co quasicrystals using realistic pair potentials had been performed by Bunz et al. [1], but the model structures they investigated proved to be stable only at very low temperatures, which was probably due to inadequate potentials. In the present work, we use new potentials derived in the framework of Moriarty's gener-

alized pseudopotential theory (GPT) [2, 3]. These GPT potentials consist of a systematic expansion into  $n$ -body terms, which is derived from first principles. For computational efficiency it is desirable to truncate this series as early as possible. Unfortunately, if transition metals (TM) are involved it is not always possible to truncate already after the two-body term, but Al-Lehyani et al. [4] have found that such a truncation is possible if a correction term is added to the TM-TM interactions. This correction term is fitted empirically to an ab-initio calculation of a simple quasicrystal approximant [4]. For computational efficiency, we have furthermore truncated these corrected pair potentials shortly after the third minimum, leading the potential functions smoothly to zero. All MD simulations were carried out with the code IMD [5] developed at our institute.

Using the same corrected pair potentials, Mihalkovič et al. [6] have developed an optimized struc-

ture model of decagonal Al-Ni-Co. In Monte Carlo simulations the model was varied until the structure with minimal energy was reached. We have used this model structure (with slight variations) also for our simulations. Since the model was optimized with respect to the same potentials, it can be expected that they fit well together, which is important for our simulations.

## 2. Stability of the model structure

The structure model of Mihalkovič et al. [6] essentially consists of an alternating stacking of two different layers, which are decorations of the same hexagon-boat-star (HBS) tiling. This results in a periodicity of about  $4\text{\AA}$ . Like in [6], we have worked with two different decorations which differ in stoichiometry. The simpler Ni-rich decoration, shown in Fig. 1, results in a composition of  $\text{Al}_{70}\text{Ni}_{21}\text{Co}_9$ , belonging to the composition range of the “basic Ni-rich” phase [7]. In the Co-rich decoration, of composition  $\text{Al}_{72}\text{Ni}_{17}\text{Co}_{11}$ , some of the Ni atoms are replaced by Co or Al (see [6]). In the following, we shall mainly concentrate on the Ni-rich decoration.

In order to check the correctness of the energy scale, we first determined the melting temperature  $T_m$ , by slowly heating the sample at constant pressure. The Ni-rich sample melted at about 1250 K, whereas the Co-rich sample melted at 1170 K. This is surprisingly close to the experimental melting temperature of the basic Ni-rich phase of about 1200 K [7], given that the potentials were originally derived for zero temperature.

Next, to check the stability of the model structures, we performed simulations at constant energy, at about  $T = 0.5T_m$ . While both structures are essentially stable, there are a few Al atoms which change their positions during the first steps of the simulation. This relaxation occurs primarily inside the stars tiles: the Al atoms there move to different positions in the quasiperiodic plane, and they moreover seek alternating positions from layer to layer, breaking the  $4\text{\AA}$  periodicity. The relaxed equilibrium positions are shown in Fig. 1. Inside the star, they depend on the number of boats around the star, which in turn is determined by the type of supertile in which the star is located (Fig. 1). Stars with one or three adjacent boats show an exact  $8\text{\AA}$

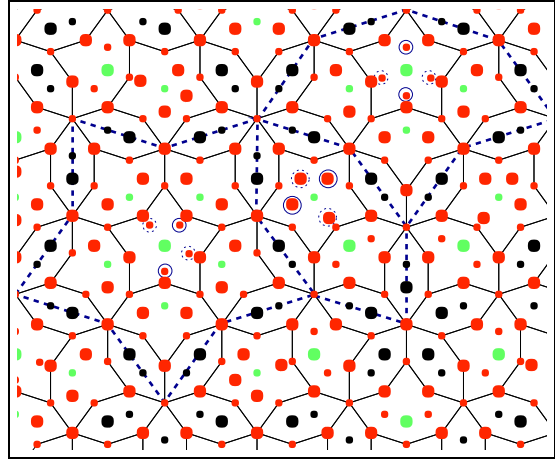


Fig. 1. Ni-rich decoration after relaxation. The positions of the marked atoms differ from the original decoration [6]. Large (small) dots indicate atoms in upper (lower) layer. Al: dark grey, Ni: black, Co: light grey. Dashed lines mark supertiles containing three characteristic local neighbourhoods of star tiles. Encircled atoms occur only in every second double layer, those with solid circles in one half of the double layers, those with dashed circles in the other half.

periodicity in equilibrium, whereas stars with five adjacent boats show an  $8\text{\AA}$  periodicity only up to about  $0.5T_m$ . At higher temperatures all of the five equivalent positions inside the star are occupied with equal probability, and the periodicity is completely broken. At very high temperatures, the decoration of the hexagon supertile as shown in Fig. 1 undergoes a further modification and becomes completely symmetric. For the following simulations, we have directly used the modified decoration corresponding the real equilibrium structure. The same modifications to the original model of Mihalkovič et al. [6] have also been observed in [8].

## 3. Diffusion of Aluminium

At temperatures above  $0.6T_m$ , significant Al diffusion is observed (Fig. 2). Only Al atoms neighboring Co atoms are involved in this diffusion, but this is a sizeable fraction of all Al atoms. Positions with mobile Al atoms are sufficiently close to each other that long range diffusion is possible. Other Al positions can remain very stable even at high temperature.

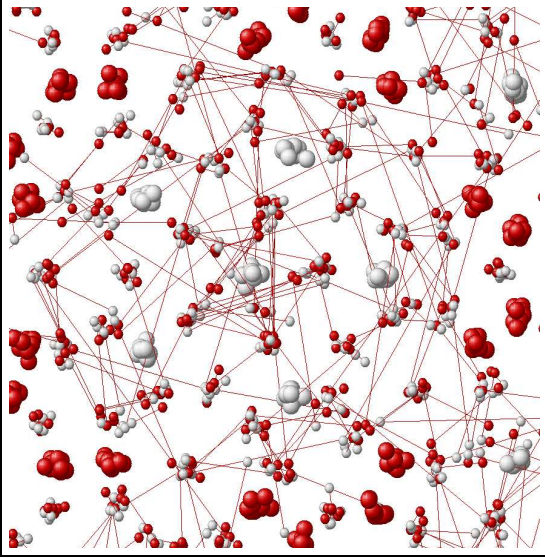


Fig. 2. Al motion at  $T = 0.9T_m$ . Dark grey, large: Ni; light grey, large: Co; dark grey, small: Al, initial positions; light grey, small: Al positions after 1ns. Initial and final Al positions are connected.

This is particularly so for Al atoms in rings with five Al and five Ni atoms, which can also be seen in (time averaged) atom density maps (Fig. 3). Al positions in these rings are very sharp, whereas those near Co atoms are completely smeared out.

At temperatures close to  $T_m$  the decoration of the supertile hexagon (a boat-star pair) is symmetric. In the atom density maps of these supertile hexagons, one can see smeared out parts of the Al distribution, namely pairs of banana shaped regions near each of the two Co atoms (Fig. 3), and continuous, zig-zag shaped distributions along the z-axis (Fig. 4), arising from the central dot in the supertile hexagon. These and other smeared out parts of the Al distribution open diffusion channels. They are sufficiently close to each other that long-range Al diffusion is possible. Similar features of the atom density maps have been observed also in [8].

Due to the high Al diffusivities, it has been possible to measure the Al diffusion constant as a function of temperature and pressure. As expected, it follows the usual Arrhenius law:

$$D = D_0 e^{-\left(\frac{\Delta H + p\Delta V}{k_B T}\right)} \quad (1)$$

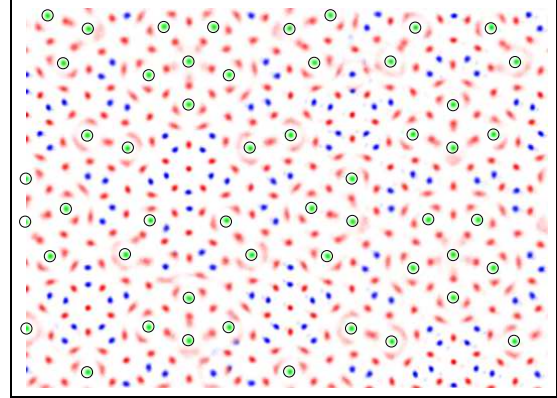


Fig. 3. Atom density map, projected on xy plane. Co positions are marked with circles; Ni positions appear as sharp, almost black dots, whereas Al positions are grayish.

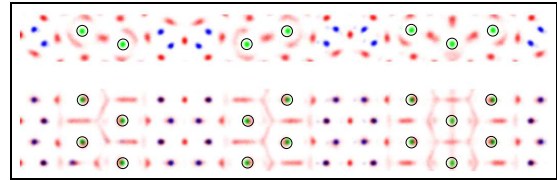


Fig. 4. Atom density map similar to Fig. 3. Here, the same slab of material is shown in projections on the xy- and the xz-plane. The central dot in a supertile hexagon consists of a continuous density along a zig-zag in the z-direction, which provides a diffusion channel.

At first we made a series of simulations with varying temperature at zero pressure. From the mean square displacements (Fig. 5) the activation enthalpies  $\Delta H$  and preexponential factors  $D_0$  could be determined, separately for the x-, the y-, and the z-direction. The resulting Arrhenius plot is shown in Fig. 6, the numerical values in Table 1. As imposed by decagonal symmetry, the diffusion is isotropic in the xy-plane.

In order to determine the activation volume  $\Delta V$ , simulations at different pressures were performed, using the Ni-rich decoration. From the decrease of the diffusivities with increasing pressure (1), the activation volume  $\Delta V$  could be determined as  $0.25(2)\Omega$  (quasiperiodic plane) and  $0.38(2)\Omega$  (z-direction), where  $\Omega$  is the atomic volume.

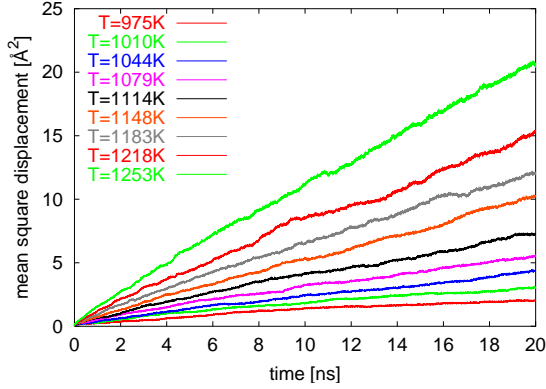


Fig. 5. Mean square displacement of Al in the x-direction as a function of time, for different temperatures (Ni-rich decoration).

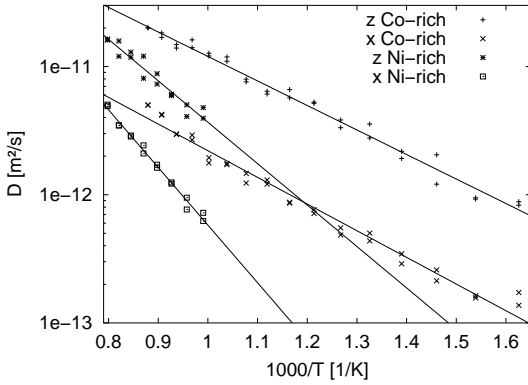


Fig. 6. Arrhenius plot for Al diffusion.

Decoration	Ni-rich	Co-rich
$\Delta H_{xy}$ [eV]	0.89(3)	0.41(1)
$\Delta H_z$ [eV]	0.64(4)	0.38(1)
$D_{0xy}$ [ $m^2/s$ ]	$1.8(4) \times 10^{-8}$	$2.6(4) \times 10^{-10}$
$D_{0z}$ [ $m^2/s$ ]	$6.2(23) \times 10^{-9}$	$9.8(8) \times 10^{-10}$

Table 1. Activation enthalpies and preexponential factors for Al diffusion. The uncertainty from the fit is given in units of the last digit.

## 4. Discussion and conclusion

Our results confirm that the model structure for decagonal Al-Ni-Co proposed in [6] is essentially stable up to the melting point. There are only minor modifications, in particular at high temperatures. A sizable fraction of the Al atoms, namely those near Co atoms, become very mobile at high temperatures, which leads to a high Al diffusivity, comparable to that of vacancy diffusion in fcc Al [9]. The diffusion we observe cannot be vacancy mediated, however. The activation volume is too small for vacancy diffusion [10]. Moreover, there are no vacancies present in the structure, and during the short simulation time vacancies cannot form. This does not exclude, however, that there is not also vacancy diffusion, if vacancies are present. Mehrer and Galler [10] have concluded that diffusion in decagonal Al-Ni-Co is predominantly vacancy mediated, as is the case for other quasicrystals. The diffusion mechanism we observe must be due to the particular (local) structure of the quasicrystal.

## Acknowledgements

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