Nucleation of quasicrystals by rapid cooling of a binary melt: A molecular-dynamics study

Johannes W. Roth*

Laboratory of Atomic and Solid State Physics, Cornell University, 532 Clark Hall, Ithaca, New York 14853-2501

Rolf Schilling

Institut für Physik, Johannes-Gutenberg-Universität Mainz, Staudinger Weg 7, 55099 Mainz, Germany

Hans-Rainer Trebin

Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Paffenwaldring 57, 70550 Stuttgart, Germany

A binary Lennard-Jones fluid was cooled in an NPT ensemble by molecular-dynamics simulations. Depending on the cooling rate, we find a sharp transition from the melt either into a disordered structure or into a phase of icosahedral long-range order. We also observed a decagonal phase.

I. INTRODUCTION

The first quasicrystals were synthesized by spin melting, and applying the right cooling rate was an important factor in Shechtman's discovery.[1] Meanwhile large single quasicrystals can be grown by the Czochralski method. But frequently a high quality ingot must be prepared first by rapid cooling of a melt and successive annealing.

From a theoretical point of view the solidification process of quasicrystals rarely has been investigated in *three dimensions*.[2,3] Most of the studies deal with simple static or dynamic growth models of *clusters*, where atoms are affixed to a given icosahedral seed.[4–7] A series of numerical simulations by molecular dynamics or relaxation algorithms[8–12] proceeds from quasicrystalline structures and test, whether they remain stable, when the atoms interact by pair potentials. In the present study we start from an unstructured Lennard-Jones melt. Hence we can monitor the *formation* and perfection of clusters, and we can be sure that nucleation and stability are not induced by a given initial state, but by factors like the short-range order of the liquid, the energy cost to create critical nuclei, and the formation enthalpy. The only previous molecular-dynamics simulation of quasicrystal solidification from the melt has been reported by Dzugutov.[3] This author has cooled a *monoatomic* liquid with a pair interaction favoring dodecahedra formation, and has indeed arrived at a dodecagonal T phase with icosahedral nearest-neighbor shells. Here we investigate diatomic systems, which are closer to experiment.

The simulations are expensive, as a large number of atoms is necessary in representing a quasiperiodic system, and as extremely long simulation runs are required to achieve low cooling rates. Those obtained still are two orders of magnitude faster than in experiment; nonetheless, for a system of 376 atoms we attained quasicrystalline "long-range" order up to at least fifth neighbors.

The paper is organized as follows. In Sec. II we describe the quasicrystalline structure model behind the simulation and the simulation method. The results of the simulation and the structure analysis are presented in Sec. III. A conclusion and discussion of related work are given in Sec. IV.

II. MODEL AND SIMULATION METHOD

First the stability and the pressure-temperature phase diagram were determined by molecular-dynamics (MD) simulations for a specific structure model of a three-dimensional icosahedral quasicrystal, namely, the truncated icosahedral binary model. Then we studied the formation of a quasicrystal from the melt. This has been done in two different ways: Either a perfect[13] quasicrystal (truncated icosahedral binary model) was melted or the atomic positions were generated by a random number generator. A subsequent cooling procedure was performed in order to solidify the system. In the first case we carefully equilibrated the melt and made sure that no correlations of the quasicrystal structure remained using the average mean square displacement. We could not find any difference in the behavior of both approaches. The analysis of the final structures showed quasicrystalline and different disordered phases, depending on the cooling rate.

The truncated icosahedral binary model is based on a three-dimensional rhombohedral quasilattice. All its vertices and edges are decorated by atoms of type A (small atoms). In addition two atoms of type B (large atoms) are placed on the long diagonal of the prolate rhombohedron, dividing it into three parts of ratios $\tau : 1 : \tau$ with $\tau = \frac{1}{2}(\sqrt{5} + 1)$. The composition of the ideal quasicrystal is $N_A : N_B = 2\tau : 1$. The model is assumed to be a simplified description of the structure of (MgZn)Al or

(AlCu)Li class quasicrystals.[9,14] The small atoms at the vertices are mostly icosahedrally coordinated, with bonds defining the fivefold directions. The small atoms at the midedge positions are also icosahedrally coordinated as a rule, but their orientation is rotated by 90° compared to the other small atoms, and so their axes point along the twofold directions. Most of the large atoms have coordination number 16, and their first-neighbor shell is a truncated tetrahedron with additional atoms above its hexagonal faces. Since we have a quasicrystalline structure, there are also other atomic environments which, however, are less important.

Boundary effects are avoided by using rational approximants. The local geometry is unchanged; only the perpendicular space structure is different. This allows us to repeat the arrangement of cells after a certain distance and to use periodic boundary conditions. The simulation cells contained 9760/3016, 2304/712, 544/168, and 128/40 A/B atoms with $\tau \approx 5/3, 3/2, 2/1$, and $1/1$. The lengths of the simulation boxes are 23.32, 14.41, 8.91, and 5.51 nearest-neighbor distances, respectively. These are the most simple cubic approximants having a set of pairwise orthogonal twofold icosahedral axes aligned with the simulation box, but it is also possible to construct more complicated approximants of different size. If the number of atoms is small, there are not so many possibilities for approximants, but usually the system finds a way to generate an ordered structure. To study the influence of the periodic boundary conditions on the orientation of the nucleated phase and on the possibility to form a quasicrystal, we simulated a structure of 288/88 atoms (length of the simulation box 7.20) which does not correspond to a simple approximant. A crystal of the Laves phase with 128/64 atoms has also been studied for comparison.

For our simulations we used the Lennard-Jones potentials

$$v_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^{6} \right],$$

where α and β equal A or B. The bond lengths $\sigma_{\alpha\beta}$ and the coupling constants $\epsilon_{\alpha\beta}$ are chosen such that the truncated icosahedral tiling is stable: $\sigma_{AA} = 1.05$, $\sigma_{AB} = 1.23$, and $\sigma_{BB} = 1.21$. The coupling constants have been set to $\epsilon_{AA} = \epsilon_{BB} = 0.656$ for same species and to $\epsilon_{AB} = 1.312$ for different species to prevent phase separations into monoatomic domains. The unit of energy will be $\epsilon_{AB} = \epsilon_0$. To save computation time we have cut off the potential at $r_c = 2.5\sigma_{AB}$. So at most steric reasons, i.e., the local atomic arrangements favored by the potential parameters, can induce the quasicrystalline order, and not specific properties of a potential like one having several minima.

The ground state of this system — for our set of potential parameters and the chosen concentration of atoms — is not known; nor is it known for similar values. But previous relaxation simulations, where the atoms were displaced at random up to 25% of their shortest distance and others where the quasicrystal was loaded with up to 20% Frenkel defects per atom, confirmed that this qua-

sicrystalline structure is at least strongly metastable for $T = 0$.[9,10]

The equilibrium MD method used to calculate the pressure-temperature phase diagram of the system requires a canonical constant-pressure ensemble (NPT) instead of the standard microcanonical one. So we modified the Hamiltonian equations by a constraint as described, for example, by Evans and Morriss.[15] The equations of motion are integrated in a fourth-order Gear predictor-corrector algorithm (see, for example, Ref. 16). The time increment δt^* (Ref. 17) was adjusted after testing for numerical stability. We find that $\delta t^* = 0.0046$ or 0.0023 are appropriate values. For simplicity the masses of small and large atoms were set to unity.

For the cooling and heating simulations we used an extension of the constraint method described by Lançon and Billard.[18] The procedure allows us to adjust the temperature (or pressure) at each time step. The cooling or heating rates were between $8 \times 10^{-10}T^*/t^* \approx 2 \times 10^7$ K/s and $8 \times 10^{-5}T^*/t^* \approx 2 \times 10^{12}$ K/s[17]. The length of a simulation run was very different depending on the cooling rate. The longest runs took up to 23×10^6 steps.

Prior to the cooling simulations we have to know the approximate "melting" curve of our quasicrystal. The melting point at a certain pressure has been determined roughly by slowly heating the system with 3016 atoms until it liquified. Then we determined the melting temperature closer by running a number of simulations at fixed temperature around the phase transition line until the structure became fluid. For $0 < P^* < 0.1$ the melting temperature T_M^* is between 0.82 and 0.93. The boiling temperature lies at $T_B^* = 1.35$ for $P^* = 0.0025$ and increases up to $T_B^* = 1.4$ for $P^* = 0.01$. From these data we decided to start our simulations in the temperature range between $T^* = 1.0$ and 1.2 at a reduced pressure $P^* = 0.0025$.

III. RESULTS

The behavior of the liquid under a cooling process is summarized in Fig. 1. Cooling from the liquid state (Fig. 1, curve 1) with rates between 10^{12} K/s and 10^{10} K/s results in a "glass" transition at about $T_G^* = 0.55$ (Fig. 1, curve 2) for all cell sizes: The slope of the potential energy vs temperature changes significantly and the diffusion of the atoms slows down from an unbounded liquidlike to a bounded solidlike behavior. Above T_G^* there is a supercooled liquid, and the thermodynamic properties, for example the potential energy or the radial distribution function, do not depend on the cooling rate. Below we find a dependence of the structure and its properties on the cooling rate, although all final structures are disordered (see Fig. 1, curve 2, where the curve for the cooling rate 10^{10} K/s is shown).

The fact that the glass temperature (and eventually the crystallization temperature) is so much below the melting transition has two reasons: First, we have periodic boundary conditions and therefore no surface, where usually the system starts crystallizing. Computer simulations have shown that solidification in such a system
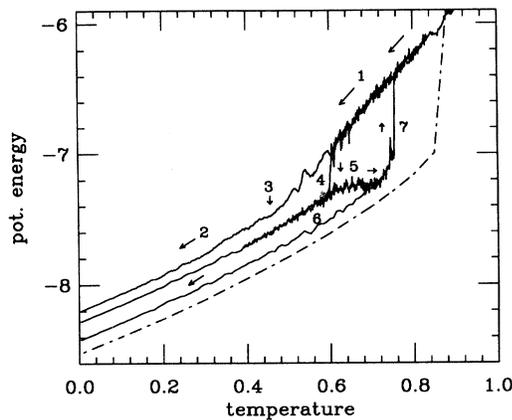
FIG. 1. Potential energy vs temperature during cooling for the system with 168 atoms. If the liquid (1) is cooled with 10^{10} K/s, we arrive at an amorphous structure (2) after a glass transition (3), which can be detected by comparing the averaged slopes on the curves of the liquid and the glass side. If the liquid is cooled with 10^9 K/s, a sharp transition (4) to a defective quasicrystal is observed. Heating it (5) improves the energy by annealing defects. The configuration with the lowest defect concentration is quenched to $T = 0$ (6) and heated until it melts (7) at a lower temperature than the perfect quasicrystal due to defects. The dashed curve shows the potential energy of a 5/3 approximant. Smaller approximants lead to the same result. The curve connects points obtained by constant temperature simulations.

requires deep undercooling.[19] Second, the system is small and a two-phase coexistence is impossible due to the large interfacial energy. Therefore the system stays solid or liquid in computer simulations until it becomes unstable as a whole.

If the cooling rate is reduced to 2×10^9 K/s, the 168-, 376-, and 712-atom structures transform sharply to an ordered solid at about $T^* = 0.6$ (Fig. 1, curve 4). The solid may still contain domains of random orientations, but the structure can be improved by annealing (Fig. 1, curve 5). The annealed phases are quenched down to $T^* = 0$ for structure analysis (Fig. 1, curve 6). The final state will be referred to as an "ordered structure."

The transition to the ordered phase also took place for a higher cooling rate between $T^* = 0.6$ and 0.5, but in that case it is not so clearly visible in the behavior of the potential energy.

In the 168-atom system there are also some cases where we observe sharp, but incomplete transitions if the cooling rate is about $5 - 10 \times 10^9$ K/s. The structure analysis shows that the nucleated phase does not fit the periodic boundary conditions. If the solid domains grow further, the defects become so severe that the structure melts again and occasionally makes a new attempt to crystallize if the temperature is not too low yet.

Constant-temperature runs with 500 000 steps at $T^* = 0.5$ and 0.4 for the ordered 168-atom system and with 20×10^6 steps at $T^* = 0.5$ for the 376-atom system as well as 13×10^6 steps for the 712-atom system show that the nucleated structures are stable. In the 376-atom case we observed that a structure, which we initially consid-

ered to be disordered, turned into a quasicrystal, and for the 712-atom case we observed a transition from the melt to a crystal with cubic symmetry and then to the "quasicrystalline ordered" phase.

If we reheat the structures obtained in the cooling runs, we see a clear difference in their behavior: The amorphous structure barely shows hysteresis. It softens and transforms back into the melt (Fig. 1, curve 3). The 168-atom system and the 376-atom system show a hysteresis loop of about $\Delta T^* = 0.12$. They melt at $T^* = 0.74$ and $T^* = 0.7$, respectively (Fig. 1, curve 7). This also demonstrates that the ordered structure has undergone a phase transition and is different from the amorphous structure where merely the dynamics has been frozen in. The melting temperature of the ordered structure is lower than that of the perfect structure since the ordered one still contains defects.

To analyze the structure of a thermodynamic state at a certain temperature we have used the standard procedure, quenching the system by a steepest gradient relaxation to $T^* = 0$ to remove the thermal displacements and the kinetic energy of the atoms. This improves the calculation of the structure functions. Further improvements have been obtained by averaging over up to 200 configurations obtained at intervals of 100 000 steps.

The structure analysis of the quenched phases reveals a long-range icosahedral order similar to that of the original quasicrystalline model. Figure 2 displays projections of the quasicrystalline ordered phase onto a plane perpendicular to the pseudofivefold axis. Although the fivefold symmetry cannot be recognized easily, one observes pentagons and rhombi similar to those in a perfect quasicrystal.

We will now describe the quasicrystalline ordered phase in more detail. It was observed in all the six runs we performed with the 168-atom structures, and three times in six attempts in the 376-atom system. The configurations were obtained in many different ways by cooling from the quasicrystalline melt, from a random configuration, and by melting, freezing, remelting, and refreezing repeatedly. Our structure analysis did not reveal any history dependence of the final state. In the 168-atom case a pairwise orthogonal set of twofold axis of the icosahedral symmetry was always aligned with the simulation box. There are two possible arrangements for the fivefold axis differing by a rotation of 90°, and we observed that during freezing, remelting, and refreezing the orientations of the fivefold axis change, which clearly rules out that the orientation is an artifact of a correlation between the nucleated phase and the original quasicrystal. It could also happen that the fivefold axis in the nucleated phase had the same or different directions when compared with the original quasicrystal. In the case of the random initial configurations obviously no correlation can exist. In the 376-atom system, also generated from random configurations, we found that the icosahedral symmetry elements could be arbitrarily oriented, one of them being nearly as aligned as in the 168-atom case. But the other two configurations show no preferred positioning relative to the simulation box. If nucleation starts and the seed grows, its boundary will eventually meet the boundary

of the seed periodically translated. If no alignment exists in the small system, the defects at the meeting point will be so severe that the structure will melt again. In the 376-atom system this does not happen. This fact clearly indicates that the system is large enough to allow an icosahedral structure, and that the icosahedral structure is not an artifact of the smallness of the system and of the periodic boundary conditions.
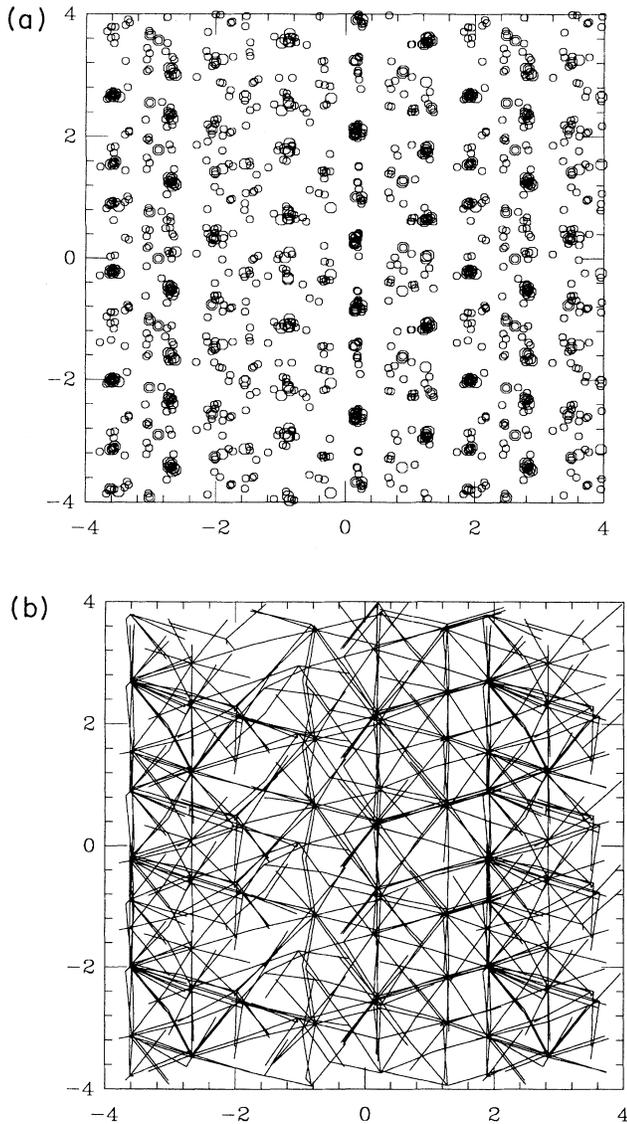
(a)

(b)

FIG. 2. Projection of the crystallized structure onto a plane perpendicular to a pseudofivefold axis. (a) Large octagons are B atoms, small octagons A atoms. The places where many octagons overlap indicate the sites of icosahedra. A pentagon displaying the fivefold symmetry can be found, for example, at the left side of the center of the figure. (b) The lines are edges of rhombohedra which point along fivefold directions. The picture is *only* periodic along the horizontal axis, but not along the vertical axis. The apparent periodicity along the vertical axis is only the result of the projection of different layers.

In the 168-atom system we also twice observed a decagonal layered structure. It will not be discussed in detail here.[20] This decagonal structure was found after cooling the *random* liquid with 2×10^8 or 2×10^9 K/s. The tenfold axis lies along a diagonal of the simulation cell, and the structure shows a periodic stacking perpendicular to this direction. The structure is distorted due to the shape of the periodic cell, but the pentagonal symmetry can be clearly seen in the projections along the periodic axis.

A. Radial distribution function and diffraction pattern

The radial distribution function (RDF) is used to study the quality of the translational order. The order becomes apparent if the RDF of an equilibrated perfect quasicrystal is compared to that of the quasicrystalline ordered and of the disordered phase (Fig. 3). Compared to the RDF of the perfect quasicrystal, the RDF of the quasicrystalline ordered phase is broadened since there are many subpeaks, which merge during relaxation due to the slightly different environment of each atom. The RDF shows at least five major peaks [Fig. 3(a)] for the AA bonds which are also present in the quasicrystalline ordered structure. The results for the distributions of AB and BB bonds are similar. We want to point out that the second peak of the AA correlation is split, but the reason is different from the splitting in amorphous structures. The two parts can be attributed to correlations in three-fold and fivefold directions. The disordered structure, however, displays only a sharp nearest-neighbor peak: the well-known split second peak and only small fluctuations at larger distances.

The translational order extends over the whole simulation cell in the 168-atom structures, which is at least of the same range as that obtained by Steinhardt *et al.*,[21] although a comparison is difficult since we have a binary structure and not a monoatomic one, and their RDF is shown only up to five atom distances. In the 376-atom system and in the 712-atom structure we have an ordering up to the same range.

Since the RDF is an average over all correlations with different directions, it cannot account for details of a specific structure; e.g., there is *no* difference visible between the RDF of the icosahedral, cubic, or decagonal ordered structures. But the amorphous structures are clearly different. The reason is that the tetrahedral close-packed structures all contain similar local atomic arrangements, which may extend up to five or more atomic distances, and so their local order is quite similar. These units can be arranged in different ways to give different global symmetries of crystalline or quasicrystalline type.

We have calculated diffraction patterns perpendicular to the pseudofivefold symmetry axis. The pattern of the quasicrystalline ordered structure [Fig. 4(b)] is pentagonal and very similar to that of the ideal icosahedral structure at $T^* = 0.01$ [Fig. 4(a)]. In the picture for the disordered structure we had to increase the intensity by a factor of 10 to make the diffraction pattern visible.

There is, however, only one ring due to nearest-neighbor ordering in Fig. 4(c); all other features are relics of the Fourier transform of the finite system.

B. Bond-order parameters

It seems to be obvious to use the bond-order parameters (BOP's) as described by Steinhardt et al.[21] and their generalization to binary structures to characterize

the orientational ordering of our structures. We find, however, that this approach fails. Hafner and Krajčí[11] have calculated the BOP's for the Henley-Elser model,[14] which is quite similar to our structure, and they find that the BOP's are not much different for the ideal structure and the equilibrated quasicrystal. We find that the BOP's for our ideal structure models are in agreement
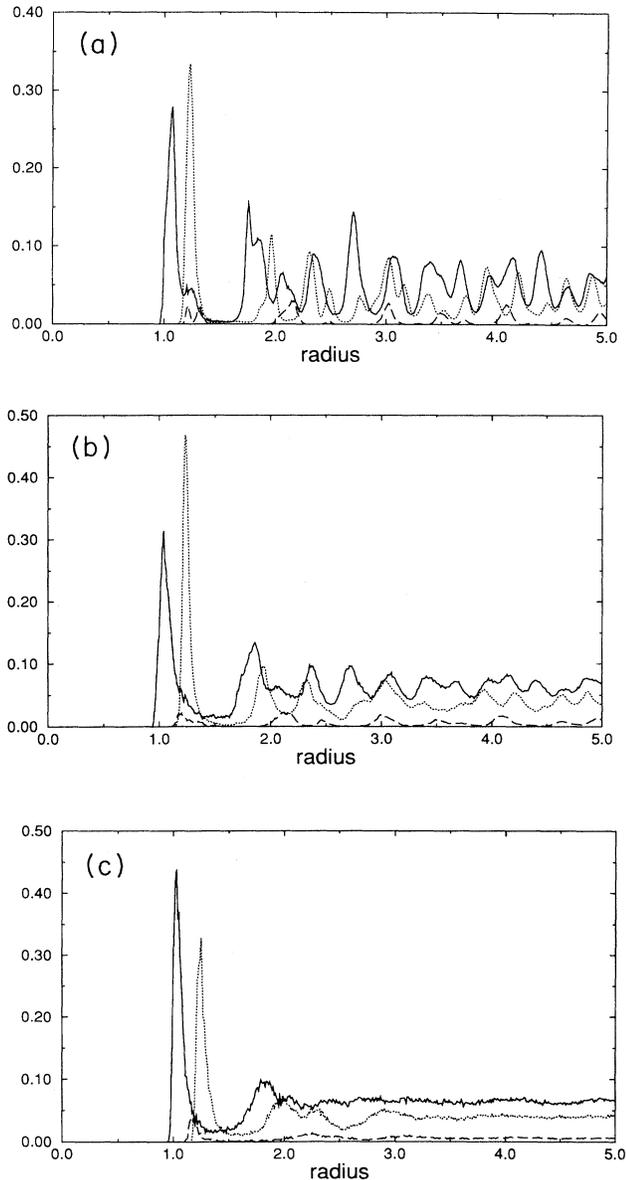

FIG. 3. (a) The radial distribution function (RDF) of the equilibrated 168-atom approximant at $T = 0.01$. Solid lines, AA bonds; dotted lines, AB bonds; dashed lines, BB bonds. The RDF of a larger approximant is largely indistinguishable. (b) The RDF of the "quasicrystalline ordered" structure. The peaks at 1.8, 2.1, 2.4, and 2.7 indicate the difference to an amorphous structure. (c) The RDF of the amorphous structure. No extra peaks appear beyond 1.7.
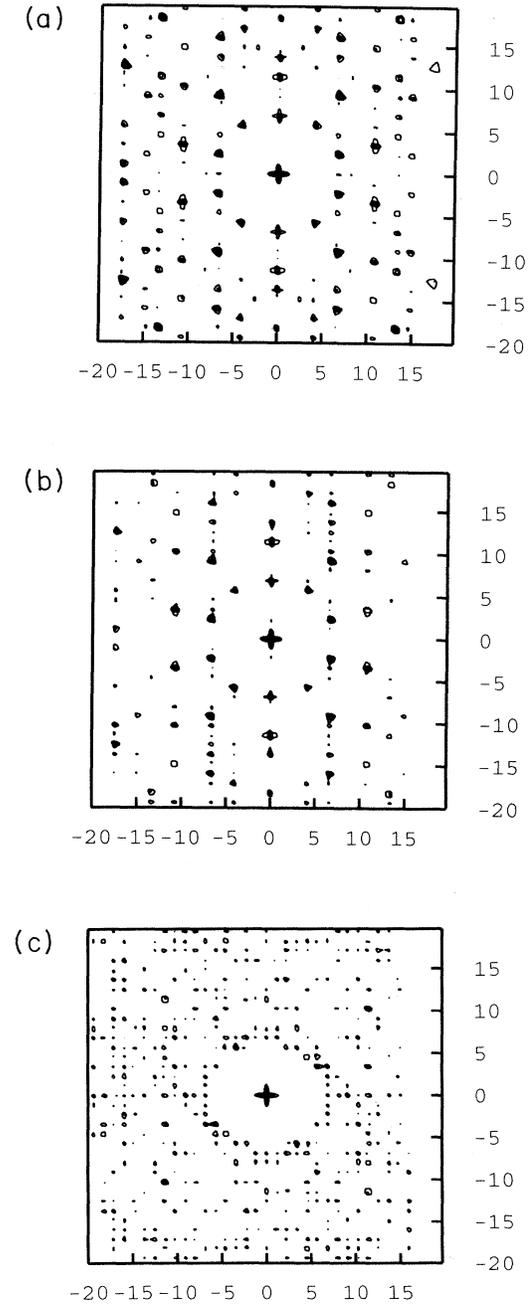

FIG. 4. Diffraction pattern perpendicular to a pseudofive-fold axis. (a) The equilibrated ideal structure. (b) The frozen "ordered" structure. (c) The amorphous structure. The intensity has been increased by a factor of 10 compared to (a) and (b).

with their result. The first problem arises if we consider structures with distortions or defects. The BOP's then decrease rapidly. Another problem is that the BOP's are strongly dependent on $1/N$, where N is the number of atoms. In general we find that $Q(2)$ and $Q(4)$ as defined in Ref. 21 are always small, $Q(6)$ is large, and $Q(8)$ is smaller than $Q(6)$, but sometimes of comparable size. This result would be consistent with icosahedral ordering, but we have to point out that there is no significant difference between the weakly disordered systems and the relaxed ideal quasicrystal. The largest values for $Q(6)$ are not found in the icosahedral structure but in the decagonal configuration obtained by freezing, and for the idealized decagonal structure model. In the cubic 712-atom structure all BOP's are small compared to the icosahedral case. Thus vanishing BOP's clearly indicate disorder, but the opposite must not be true. Part of this problem stems from the fact that we have a rather complicated structure. In fcc, hcp, or bcc crystals and in the icosahedron one has 12–14 bond directions. In our structure we have more than 40 major bond directions and 140 minor ones in the perfect quasicrystal. Therefore the BOP's are very sensitive to small deviations from the ideal orientation.

C. Further characterization

We have developed a method which can help to find out if a certain structure is ordered or disordered and also to find its symmetry. A histogram of the nearest-neighbor bond distribution is mapped onto the surface of a sphere, thereby keeping the direction of the bonds as it is in the structure. Expanding the distribution into spherical harmonic functions would give us the bond-order parameter. Instead, we display the sphere graphically. The sphere is half transparent which allows one to see the bonds at the back side also. The sphere can be rotated until a symmetry axis is found. Figure 5 shows some examples. With the graphical method we could immediately recognize which of our structures were ordered and if they had certain symmetry axis. After the first symmetry elements are found it is easy to determine the whole symmetry by using their geometry relations.

Both the bond-order parameter (BOP) and the graphical representation contain the same information. The former one is just the expansion of the latter with respect to the spherical harmonics. However, we found that the bond orientational order reveals itself much better in the graphical representation. This is due to the fact that for the BOP many of the lower-order terms vanish due to symmetry; others are very small since the major bond directions point to the zeros of the spherical harmonics. The remaining terms of usually higher order are not very accurate for small structures. Therefore the BOP's give only a crude approximation of the picture seen in the graphical representations.

A second step involves building models of the frozen structure. This has been done for the 168-atom system. The bonds between neighboring atoms in the quasicrystalline ordered structure point along fivefold, threefold,

and twofold symmetry axes or lie in the mirror planes of the icosahedral symmetry. The fivefold bonds (and the twofold ones to a lesser extent) are the only ones that can easily be distinguished from the others. In the tiling description they point along the edges and face diagonals of the rhombohedra in the perfect quasicrystal. We can therefore use them to set up a network of fivefold bonds and to reconstruct the original tiling. In the perfect quasicrystal *all* A atoms lie on the vertices and edges of the rhombohedra and therefore on the network. In the quasicrystalline ordered phase the fraction is still 96%. All the B atoms had been placed on the long body diagonal of the prolate rhombohedra. After the simulation we find 75% of the B atoms on these diagonals.

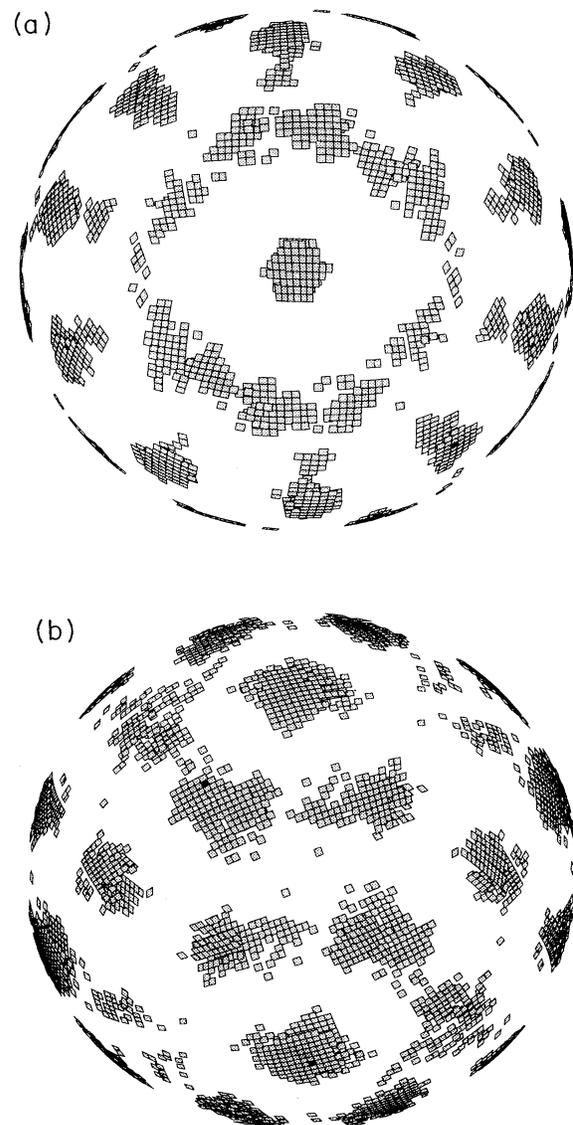Using the atomic positions of the frozen structure we

FIG. 5. Example of a bond histogram on a sphere. (a) A fivefold axis of a 376-atom system. (b) A fourfold axis of the 712-atom structure.

determined the atoms that would lie on a tiling as defined by the ideal structure model. We started at an arbitrary atom and added all atoms to a network which had five-fold bond connections not deviating by more than 2% from the ideal length and orientation. With this information we have built models with balls that allow only icosahedral bonds and rigid sticks of unit length. The models show that the quasicrystalline ordered structure is composed of the original rhombohedra and of rhombic dodecahedra, which consists of two prolate and two oblate rhombohedra. Some of the faces and edges are not complete, and there are also matching rule violations, but essentially we have found a section of an icosahedral tiling with about 30 rhombohedra. If we use an alternative description of the structure in terms of tetrahedra, prisms, pyramids, and octahedra, which are defined by including the twofold bonds as edges, about 72% of the simulation cells can be attributed to the tiling.

Before annealing the defect density is quite high: We find almost no complete rhombohedra. If one tries to complete the fragments, the additional cells will interpenetrate.

The perfect quasicrystal may alternatively be described in terms of Frank-Kasper (FK) polyhedra.[22] In the ideal quasicrystal the large B atoms have a 16-fold coordination (CN16), and most of the A atoms are icosahedrally coordinated. The same structure is found in the quasicrystalline ordered phase. However, the arrangement of the FK polyhedra may be different, which makes it impossible to combine them into rhombohedra. Closely related to our model is the cubic crystalline Laves phase $C15$, for example the structure of $MgCu_2$. It consists of the same CN16 blocks, but instead of the icosahedra of A atoms at the corners of the rhombohedra there are only tetrahedra present in $C15$. The Laves phase can be decomposed into prolate rhombohedra which are slightly distorted with respect to icosahedral geometry. We find that this phase has a potential energy lower than the perfect quasicrystal if we apply the same potential parameters as for the cooling simulations. We do not know, however, if the structure is indeed more stable, since this would require us to know the chemical potentials for the Laves phase and the icosahedral phase. A certain tendency to form the $C15$ phase can be found in the quasicrystalline ordered phase at places where equally oriented prolate rhombohedra meet. In the 712-atom simulation we find that a highly defective $C15$ phase is nucleated first. But after annealing the structure for about 13×10^6 steps it transforms into a still defective quasicrystalline structure. It is remarkable that the simulation of the crystalline Laves phase with 192 atoms and with potential parameters that favor an icosahedral model also resulted in a quasicrystalline structure.

IV. DISCUSSION AND CONCLUSIONS

The dodecagonal quasicrystal obtained by Dzugutov[3] is a *monoatomic* system of 16 384 atoms. His structure also contains FK-type atom shells. He used a potential with a maximum and two minima to stabilize the structure. Liu and Wang[2] on the contrary only got what they call an "amorphized quasicrystal" by cooling a binary melt with 500 atoms at a rate of 2×10^{10} K/s. They used effective potentials and compositions which should model a $Al_{0.86}V_{0.14}$ quasicrystal. We have found a formation of a quasicrystalline structure for up to 712 atoms, whereas the larger models could not be treated with low enough cooling rates up to now. This clearly indicates the fact that it is much more difficult to get a binary quasicrystal from a melt than a monoatomic one, since in the binary case the atoms must be chemically ordered, whereas all atoms are equivalent in the monoatomic model. It also seems important that the interaction in binary systems must be of longer range than in monoatomic systems, since otherwise the structure often behaves like a monoatomic system and crystallizes into a bcc or fcc crystal structure. Dzugutov's mechanism for stabilization of the quasicrystalline structure is the special potential which prevents the creation of fcc, hcp, and bcc nearest-neighbor arrangements. In his case the influence of the cooling rate is not known, in contrast to our model where the very low cooling rate plays a crucial role.

It may seem as if our system is too small to describe a real quasicrystal. We point out, however, that in the 168-atom structures the symmetry elements of the icosahedral structure still had to be aligned with the simulation box. But already in the 376-atom system they could be oriented arbitrarily. Finally in the 712-atom system we found a transition from a *crystalline* state to a defective *quasicrystalline* structure. Very recently Tsay and Liu[23] have shown for a monoatomic system that the periodic boundary conditions do not affect nucleation and final structure from their maximum value of 3500 atoms down to 500 atoms. If we apply this observation to our binary structure, it indicates that our results are not artifacts of the small system size.

The fact that we have a *binary* system is also important to prevent a simple crystal structure. We have chosen the potential parameters in such a way that local atomic arrangements in the quasicrystal are favored, and dense-packed structures like fcc, hcp, or bcc are disfavored. Usually the structure obtained in this way is a glass, not a crystal.[24] A Frank-Kasper crystal of the $MgCu_2$ type as described above, however, has a structure similar to the ideal quasicrystal and a defective structure of this type can be formed intermediately, as was observed by us for the 712-atom structure. The Frank-Kasper phase is more stable than the quasicrystal at its proper composition. But in our simulations we have too many small A atoms which lead to high-energy defects in the crystal and thus destabilize it. In monoatomic systems one must choose very high cooling rates to prevent crystallization, whereas in the binary system one usually gets a glass even for rather low cooling rates. For the nucleation of a crystal one really needs very low cooling rates. Therefore it might be that our cooling rates are much too high to allow a periodic crystal.

Before we describe our results in the context of icosahedral glass models, we have to clarify the notation. There is, for example, the icosahedral glass model as studied by

Steinhardt *et al.*[21] for monoatomic and by Jónsson and Anderson[24] for binary structures. The authors are interested in the local icosahedral nearest-neighbor ordering but they do not study the global symmetry of the structure as we did with the bond diagrams. Jónsson and Anderson find relatively few icosahedra in their diatomic simulations. In a 1500-atom system they find 61% of the atoms located in icosahedra and one spanning cluster of icosahedra. In a 500-atom simulation they find less icosahedra. For comparison, in our simulations only 50% of the small atoms are located in the icosahedra. It is not possible to have much more since we have a binary structure where the large atoms want to be 16-fold coordinated. There is not only a spanning cluster but a three-dimensional connected network which can be part of a tiling. This leads us to the other type of icosahedral glass model or, better, icosahedral cluster model. Our simulation results certainly do not describe a perfect icosahedral tiling or even a random tiling, which is defined as a random arrangement of tiles without gaps. Such a result cannot be expected and also has not been found in two dimensions.[8] But if we drop the requirement of a gapless tiling, we arrive at the icosahedral cluster model, which is defined as a random arrangement of icosahedral clusters with fixed orientation, thus leading to a network and a tiling with gaps.

In this framework we can describe our results as be-

tween the two icosahedral glass models, although a more quantitative comparison is not possible due to the limited information in the data of Steinhardt *et al.* Compared to their results we obtained a much larger icosahedral orientational ordering. But our clusters are not perfectly oriented, since we have defects and distortions which cannot be prevented in a finite-temperature simulation. To make a final decision as to which model fits better we would have to test by what power of the particle number the intensity of the diffraction peaks is increasing or by what algebraic law the bond-orientation–correlation function is decaying in a finite-size scaling analysis. This would require structures spanning several orders of magnitude. But our current computing power and algorithms do not allow it.

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* Permanent address: Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Paffenwaldring 57, 70550 Stuttgart, Germany.

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