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Concerted Molecular Displacements in a Thermally-Induced Solid-State Transformation in Crystals of DL-Norleucine

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Abstract: Martensitic transformations are of considerable technological importance, a particularly promising application being the possibility of using martensitic materials, possibly proteins, as tiny machines. For organic crystals, however, a molecular level understanding of such transformations is lacking. We have studied a martensitic-type transformation in crystals of the amino acid DL-norleucine using molecular dynamics simulation. The crystal structures of DL-norleucine comprise stacks of bilayers (formed as a result of strong hydrogen bonding) that translate relative to each other on transformation. The simulations reveal that the transformation occurs by concerted molecular displacements involving entire bilayers rather than on a molecule-by-molecule basis. These observations can be rationalized on the basis that at sufficiently high excess temperatures, the free energy barriers to concerted molecular displacements can be overcome by the available thermal energy. Furthermore, in displacive transformations, the molecular displacements can occur by the propagation of a displacement wave (akin to a kink in a carpet), which requires the molecules to overcome only a local barrier. Concerted molecular displacements are therefore considered to be a significant feature of all displacive transformations. This finding is expected to be of value toward developing strategies for controlling or modulating martensitic-type transformations.

Introduction

Martensitic transformations are first-order crystal−crystal phase transitions that proceed rapidly without diffusion of the atomic or molecular species. They exhibit a displacive structural change that gives rise to a shear-like deformation of the crystal morphology and can be characterized by a definite orientational relationship between the lattices involved.[1−4] Such transformations are observed in metals, alloys, and ceramics,[3] as well as in molecular crystals[5] and proteins.[6] A remarkable example of a martensitic transformation in a protein crystal is the injection mechanism of the T4 bacteriophage virus, where the tail-sheath protein of the virus contracts by a martensitic mechanism to puncture the bacterial membrane, enabling the virus to inject its DNA content.[6] Martensitic transformations are of considerable technological importance and applications include smart materials based on shape memory effects,[7] flexible wires resulting from superelasticity associated with the transformation,[8,9] and self-healing ceramics.[10] A particularly promising application is the possibility of using martensitic materials, possibly proteins, as tiny machines[11] that could, for example, deliver genes or drugs to specific sites within the body. Although a phenomenological theory for martensitic transformations is well developed,[3] the molecular mechanism by which these transformations occur is still not fully resolved. Although it is generally accepted that martensitic transformations in metals, alloys, and ceramics involve perfectly correlated displacements of large numbers of atomic or molecular species, there is no consensus that such processes occur in martensitic-type transformations in molecular crystals. We report here observations from molecular dynamics simulations of concerted molecular displacements in a martensitic-type transformation in crystals of the amino acid DL-norleucine. We show by means of potential energy barrier calculations and theoretical considerations that concerted molecular displacements are feasible and indeed expected in such transformations in molecular crystals.

A key issue concerning first-order crystal−crystal phase transformations is the nature of the molecular processes taking place during the transformation, in particular at the interface between the parent crystal and the emerging new phase. This issue remains essentially unresolved, as there is little direct

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(1) Cohen, M. *Trans. Japan Inst. Metals* **1988**, *29*, 609−624.
(2) Olson, G. B.; Owen, W. S. *Martensite*; ASM International: Materials Park, OH, 1992.
(3) Christian, J. W. *The Theory of Transformations in Metals and Alloys*, 3rd ed; Elsevier Science Pub Co.: New York, 2002.
(4) Bhadeshia, H. K. D. H. *Worked Examples in the Geometry of Crystals*; Institute of Materials: London, 2001.
(5) Mnyukh, Y. V.; Panfilova, N. A.; Petropavlov, N. N.; Uchvatova, N. S. *J. Phys. Chem. Solids* **1975**, *36*, 127−144.
(6) Olson, G. B.; Hartman, H. *J. Phys*. **1982**, *43*, 855−865.
(7) Otsuka, K.; Ren, X. B. *Intermetallics* **1999**, *7*, 511−528.
(8) Otsuka, K., Wayman, C. M., Eds. *Shape Memory Materials*; Cambridge University Press: Cambridge, 1998.
(9) Funakubo, H., Ed. *Shape Memory Alloys*; Gordon Breach Sci. Pub.: New York, 1987.
(10) Kelly, P. M.; Rose, L. R. F. *Prog. Materials Sci*. **2002**, *47*, 463−557.
(11) Bhattacharya, K.; James, R. D. *Science* **2005**, *307*, 53−54.

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experimental evidence to support any of the hypotheses that have been proposed. Methods such as X-ray diffraction are still, in general, unable to yield the molecular trajectories at the interface because of temporal and spatial averaging, although for specific systems techniques such as grazing incidence are beginning to yield near atomic resolution.[12] Theoretical ideas regarding the molecular mechanism of these phase transformations are dominated by the structural classification proposed by Buerger.[13] In Buerger's scheme, transformations are classified on the basis of similarity (or otherwise) between the crystal structures of the phases involved. An integral part of the scheme is the relationship between the differences in structure (and the changes perceived in going from one structure to another) and the energy barriers determining the kinetics of the transformation. If the crystal structures are relatively similar and the new lattice may be generated by a simple differential dilation of the parent lattice or by minor displacements or rotations of the molecular species, the transformation is classified as either dilational or displacive, respectively. As there is no making or breaking of strong interactions, the energy barriers are considered to be low and the transformation kinetics rapid. If significant reorganization of the molecular species is involved, the transformations are classified as reconstructive and are characterized by a high-energy barrier and hence expected to be sluggish. Using Buerger's classification as a basis, it has become common practice to describe the mechanism of dilational or displacive transformations as comprising a series of cooperative lattice translations and/or orientations based on least motion.[14,15] For molecular crystals, the proposed mechanistic approach is more complex, involving displacement and rotations of the molecular species.[16,17]

Hartshorne and co-workers[18] took a different approach and focused on the molecular processes at the interface. They proposed the existence of an intermediate vapor phase, with molecules subliming from the parent phase and condensing on to the new daughter crystal. This hypothesis is, however, difficult to reconcile with experimental data, as the observed kinetics of interface advance are significantly faster than predicted. An extension of these ideas was the proposal of a dual mechanism: a cooperative, displacive mechanism within the crystallites, and sublimation and condensation between the crystallites.[19]

A significant advance has come from the insights of Mnyukh and co-workers[20] from their work on single crystals of molecular systems. They propose that the transformation process for first-order crystal−crystal transformations is essentially analogous to crystallization of the new phase but from a solid medium, and where there is a scope for a coherent interface between the parent and the daughter phase, this can lead to the possibility of an orientational relationship (topotaxy) between the two

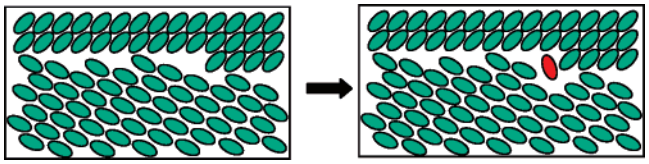

Figure 1. Contact interface mechanism (after Mnyukh[20]). In this mechanism, interface advance is considered to proceed by the detachment of a molecule from the parent phase and subsequent attachment onto the emerging surface of the daughter phase, i.e., on molecule per molecule basis. The transferring molecule remains within the interaction field of both lattices at all times.

lattices. They consider that the interface between the parent and daughter phase is characterized by direct contact, and more contentiously, that the molecules belonging to the parent phase re-align themselves *one-by-one* onto the developing surface of the daughter crystal. The process is depicted in Figure 1. This proposed mechanism specifically excludes any form of cooperative behavior of the molecules on the basis that the one-by-one re-alignment at the interface is energetically appealing.[5,21] The analogy commonly promoted is the difficulty encountered in shifting a large carpet wholesale across the floor. The contact interface hypothesis also emphasizes the important role (which is well recognized) of clusters of vacancy defects in both initiating the transformation and in its continuation.

The one-by-one hypothesis, however, fails to explain the observed, specific crystal deformation characteristic of martensitic transformations in metals and alloys. Uncoordinated atomic displacements are unlikely to induce any net motion or net force in any particular direction in the crystal and, consequently, can only give rise to a general change in volume and not any specific deformation. Any specific deformation of the crystals is considered to be a direct consequence of collective synchronized atomic displacements.[4] There are some rare examples of molecular crystals that exhibit the thermosalient effect, the phenomenon of crystals jumping during a phase transition.[22−24] This phenomenon is thought to occur as a result of an abrupt specific deformation of the crystal, and from the above argument, the implication is that concerted molecular displacements are involved.

We have investigated a martensitic-type transformation in crystals of the amino acid DL-norleucine (2-aminohexanoic acid, $CH_3(CH_2)_3CH(NH_2)COOH$) by means of classical molecular dynamics simulations. DL-norleucine is one of very few molecular crystals that exhibit a fast single-crystal to single-crystal transformation with an orientational relationship. It can crystallize in three polymorphic forms, α, β, and γ. The β form is the low-temperature phase, known to be stable at about 120 K.[25] It can transform reversibly to the α form (the transition temperature is not stated in the literature), which is the stable phase at room temperature and pressure. Above 390 K, the α form exhibits a reversible transformation to the high-temperature γ form.[5] The crystal structures of the α and β forms are known,[25−27] the lattice parameters being SG = $P2_1/a$, $Z = 4$, a

(12) Solomonov, I.; Weygand, M. J.; Kjaer, K.; Rapaport, H.; Leiserowitz, L. *Biophys. J.* **2005**, *88*, 1809−1817.
(13) Buerger, M. J. *Kristallographia* **1971**, *16*, 1048; Buerger, M. J. *Soviet Phys.: Crystallogr., USSR* **1972**, *16*, 959.
(14) Swaminathan, S.; Srinivasan, S. *Acta Cryst.* **1975**, *A31*, 628−634.
(15) Pendas, A. M.; Luana, V.; Recio, J. M.; Florez, M.; Francisco, E.; Blanco, M. A.; Kantorovitch, L. N. *Phys. Rev. B* **1994**, *49*, 3066−3074.
(16) Hashizume, D.; Miki, N.; Yamazaki, T.; Aoyogi, Y.; Arisato, T.; Uchiyama, H.; Endo, T.; Yasui, M.; Iwasaki, F. *Acta Cryst. B* **2003**, *59*, 404−415.
(17) Fernandes, M. A.; Levendis, D. C.; Schoening, F. R. L. *Acta Cryst. B* **2004**, *60*, 300−314.
(18) Bradley, R. S.; Hartshorne, N. H.; Thackray, M. *Nature Lond.* **1954**, *173*, 400.
(19) Briske, C.; Hartshorne, N. H. *Trans. Farad. Soc.* **1967**, *63*, 1546,
(20) Mnyukh, Y. V.; Petropavlov, N. N. *J. Phys. Chem. Solids* **1972**, *33*, 2079.
(21) Mnyukh, Y. V. *Fundamentals of Solid-State Phase Transitions, Ferromagnetism and Ferroelectricity*; Authorhouse: Bloomington, IN, 2001.
(22) Steiner, T.; Hinrichs, W.; Saenger, W.; Gigg, R. *Acta Cryst.* **1993**, *B49*, 708−718.
(23) Zamir, S.; Bernstein, J.; Greenwood, D. J. *Mol. Cryst. Liq. Cryst.* **1994**, *242*, 193−200.
(24) Lieberman, H. F.; Davey, R. J.; Newsham, D. M. T. *Chem. Mater.* **2000**, *12*, 490−494.
(25) Dalhus, B.; Gorbitz, C. H. *Acta Cryst.* C **1996**, *52*, 1761−1764.

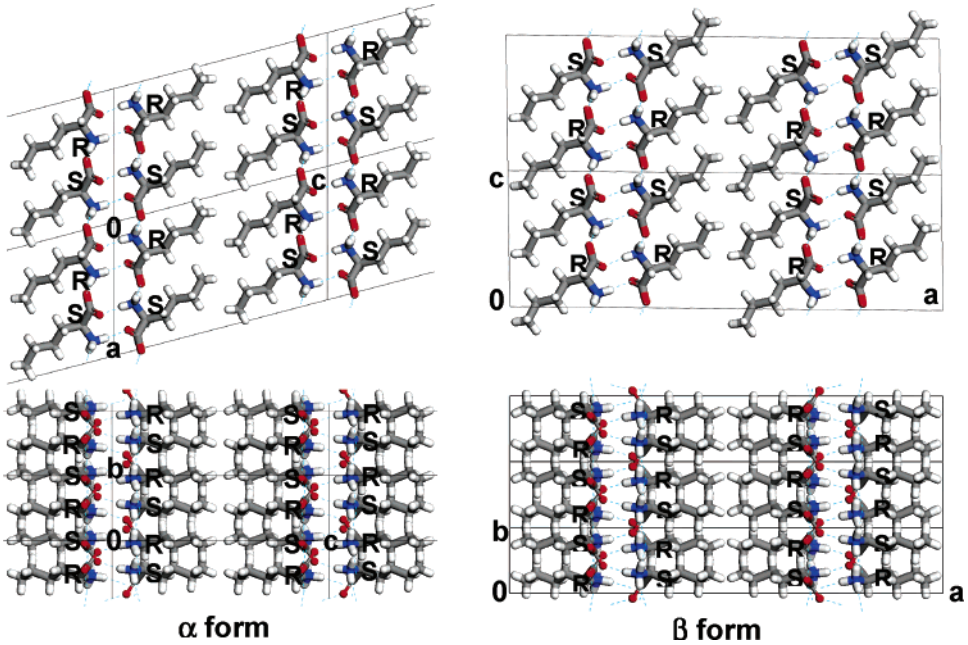

Figure 2. Crystal structures of the α-phase (space group $P2_1/a$) and β-phase (space group $C2/c$) of DL-norleucine showing the van der Waals surface between hydrogen-bonded bilayers. The structures are racemates containing chiral molecules (designated by R and S) that do not interconvert on laboratory time scale. The *c*-axis in the α-phase corresponds to the *a*-axis in the β-phase. For the α-form, the sequences along the *c*-axis in the *b*−*c* perspective alternate between RSRS and SRSR as we go up the *b*-direction. For the β-phase the corresponding sequence (along the *a*-axis) is RSSR, which alternates with SRRS as we go up the *b*-direction. In the *a*−*c* perspective of the α-phase, a particular sequence of molecules along the *c*-axis has the same sense of chirality, e.g., SSSS that alternates with RRRR going in the *a*-direction. The corresponding sequences (direction [101]) in the β-phase are SSRR and RRSS. The α-phase structure can be obtained from the β-phase by a *b/2* shift along the *b*-axis and *c/2* along the *c*-axis of one of the bilayers of the β-phase. The *b/2* shift changes the RSSR sequence to the required RSRS sequence, whereas the *c/2* shift changes the SSRR and RRSS sequences to SSSS or RRRR, which are characteristic of the α-phase. The bar notation on the sequences represents recurrence.

= 9.907 Å, *b* = 4.737 Å, *c* = 16.382 Å, β = 104.68°, ρ = 1.171 Mg m^{-3}, and SG = *C*2/c, *Z* = 8, *a* = 31.067 Å, *b* = 4.717 Å, *c* = 9.851 Å, β = 91.37°, ρ = 1.207 Mg m^{-3} for the α and the β forms, respectively. Both crystal structures are racemates with equal numbers of the (*R*) and (*S*)-norleucine molecules. In both phases, the norleucine molecule is in the zwitterionic form with an almost identical geometry in terms of bond lengths, bond angles, and dihedrals, whereas the molecular packing in the crystals is in the form of bilayers, which is typical of amino acids. The bilayers are formed by virtue of tight hydrogen bonding between the $-COO^-$ and $-NH_3^+$ groups both within a layer and between the layers. The outer surfaces of each bilayer comprise the ends of the aliphatic chains that give rise to a van der Waals surface between one bilayer and the next. The two crystal structures differ in that in the α form the alternate bilayers are shifted by half a unit cell along both the *b*- and *c*-axis relative to the packing in the β phase (Figure 2).

Methodology

The molecular dynamics simulations were carried out on a periodic system comprising 800 independent molecules (equivalent to 2 × 10 × 5 unit cells of the β phase) in an NPT ensemble with Parrinello-Rahman boundary conditions[28] using the program DL_POLY.[29] The potential parameters employed were those optimized by us earlier to reproduce the crystal structures of the α and β forms and the $\beta\rightarrow\alpha$ transformation.[30] We investigated the $\beta\rightarrow\alpha$ transformation at various temperatures up to 390 K and also explored the effects of inclusion of vacancy defects. The electrostatic interactions were evaluated using Ewald summation with a precision of 1.0×10^{-6} (Ewald convergence parameter = 0.4051, and maximum *k*-vectors of 13, 8, and 8 in the three axis, *x*, *y*, and *z*). The interaction cutoff for both the van der Waals and the real part of Ewald was 1.0 nm. Appropriate long-range corrections for the truncated van der Waals interactions were applied to both the potential and the instantaneous pressure. The effects of various technical variables such as the thermostat and barostat coupling constants and the choice of flexible bonds or bond constraints were also explored.

We also characterized the potential energy barrier that defines the phase transformation, namely the barrier to shifting of an entire bilayer relative to the rest of the crystal. These potential energy surface calculations were carried out on a periodic system comprising two independent bilayers each comprising 60 molecules. The energy surface for the bilayer shift was sampled by means of a grid search where the lattice was dilated along the axis perpendicular to the bilayers (the *a*-axis of the β phase) by a series of 0.2 Å increments, and for each dilation one of the bilayers was systematically shifted in 0.2 Å increments along the other two axes (the *b*-axis and *c*-axis of the β phase), i.e., in the plane parallel to the bilayer. At each shift position, the potential energy of the system was minimized while maintaining a spatial constraint on the α carbon. The minimum energy surface as a function of the bilayer shift position was taken to be the lowest energy obtained from the series of lattice dilations at that shift position.

Another important quantity that is pertinent to the thesis developed in this paper is the potential energy required for a molecule to move from a lattice site into an adjacent vacancy defect. In determining this energy, four localized vacancy defects were created in one surface of

(26) Mathieson, A. M. *Acta Cryst.* **1953**, *6*, 399−403.
(27) Harding, M. M.; Kariuki, B. M.; Williams, L.; Anwar, J. *Acta Cryst.* **1995**, *B51*, 1059−1062.
(28) Parrinello, M.; Rahman, A. *J. Appl. Phys.* **1981**, *52*, 7182−7190.
(29) Smith, W.; Forester, T. R. *J. Mol. Graphics* **1996**, *14*, 136.
(30) Tuble, S. C.; Anwar, J.; Gale, J. D. *J. Am. Chem. Soc.* **2004**, *126*, 396−405.

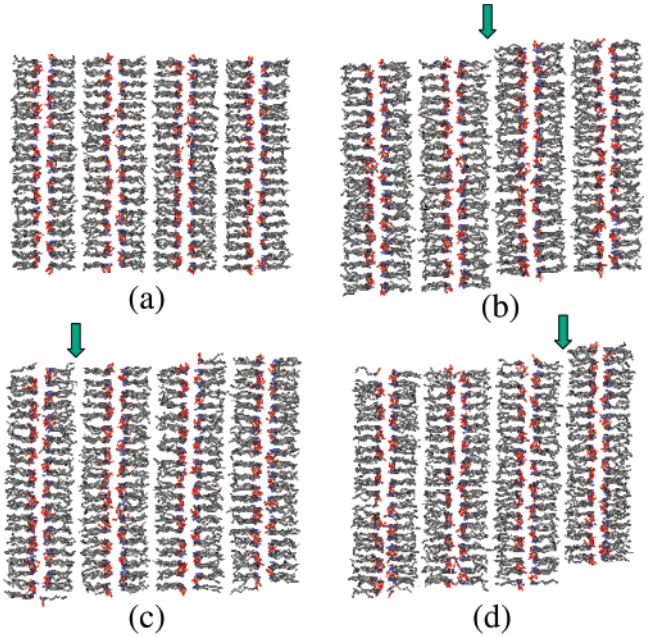

Figure 3. Snapshots from the molecular dynamics simulation trajectory of the transformation of the β-phase of DL-norleucine at 390 K and ambient pressure. (a) 200 ps, (b) 320 ps, (c) 400 ps, and (d) 500 ps. The system is periodic in all three dimensions and comprises 800 independent molecules. The hydrogen atoms have been removed from the molecules to aid structural clarity. The arrows highlight the bilayer shifts.

one of the bilayers, and the interaction energy of a single molecule was sampled as a function of its displacement tangential to the bilayer into the vacancy.

Results and Discussion

Snapshots of the molecular dynamics trajectory at 390 K showing the various stages of the transformation are shown in Figure 3. The trajectory reveals a remarkable, synchronized displacement of all molecules within any given bilayer relative to another bilayer, i.e., a shift in the entire bilayer. The transformation is initiated by the wholesale shifting of the bilayers at the van der Waals surface in the middle of the simulation cell. This is then followed by a shift at the adjacent van der Waals surface on one side of the initial labile interface and then at the other. There is no nucleation event wherein the transformation would be initiated at some local hot spot in the lattice and then spread out. Structurally, the transformation does not appear to yield the true α-phase. The transformation proceeds, as expected, by the shifting of the bilayers at the van der Waals surfaces but the observed shift is only half a unit cell along the *b*-axis (expected) without a corresponding shift along the *a*-axis. The system appears to adopt an alternative packing at the van der Waals surfaces, presumably as a result of the potential parameters not being sufficiently accurate to characterize the weak interactions at the van der Waals surfaces. The observed structure could possibly be the γ-phase whose structure still remains unresolved and is considered to be a variation on the packing at the van der Waals surfaces between the bilayers. The lattice parameters of the simulated phase were $a \approx 17.8$ Å, $b \approx 5.1$ Å, $c \approx 10.5$ Å, $\beta \approx 110°$.

A simulation of the crystal with four localized vacancy defects also revealed shifting of entire bilayers during the transformation. The vacancies can serve as sites of nucleation as the activation energy here is likely to be lower and this effect has been observed in molecular dynamics simulations of other systems.[31] A simulation of the system containing 4 adjoining *rows* of vacancies was also carried out. In this case the vacant rows indeed did serve as the initiation point, with the bilayer containing the vacant rows being the first to shift. We expected that the *individual* molecules in that bilayer adjacent to the vacancy rows would translate into the vacancies and in so doing would leave behind vacancies that would then in turn be filled with the next set of molecules, i.e., the transformation should show a molecule-by-molecule or a molecular row-by-molecular row behavior. This was not observed. Instead, as in the other simulations, the entire bilayer adjacent to the row of vacancies shifted wholesale. Snapshots from the trajectory of this simulation are given in the Supporting Information. In all the simulations, any particular bilayer shift, when it did take place, occurred extremely rapidly, being over in about 20 ps. Once initiated, the required shifting of the bilayers to cause the full transformation of the crystal took about 200 ps at 390 K. As the size of the simulation system is modest (but respectable, containing 16 800 atoms) and only a few simulations have been carried out, it is not possible to get a good estimate of the interface velocity. A rough calculation yields an interface velocity (the direction of interface advance being perpendicular to the van der Waals surfaces) of about 35 m/s, based on the fact that the full transformation of the crystal involved an interface advance of 4 cell lengths of the α-phase along the

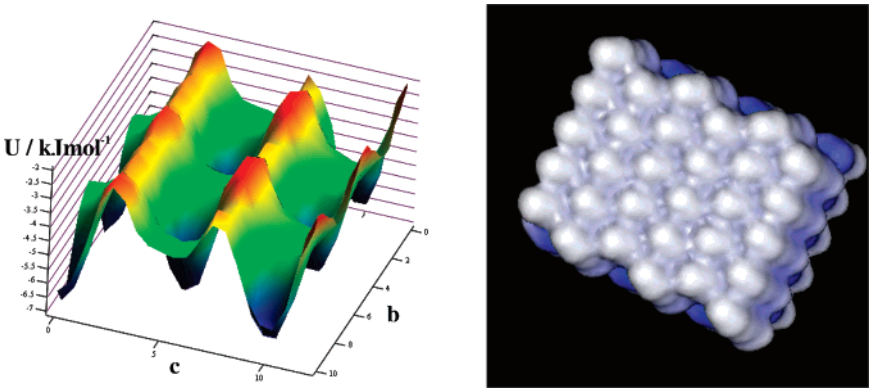

Figure 4. Potential energy surface for the translation of one bilayer within a crystal of DL-norleucine and the corresponding physical van der Waals surface. As expected there is a strong correspondence between the two surfaces with the indentations in the physical surface corresponding to the energy minimum in the potential energy surface. The energy surface for the bilayer shift was sampled by means of a grid search comprising 0.20 Å increments with energy minimization at each position.

a-axis in 200 ps, i.e., about 7.1 nm in 200 ps. This is high but expected as the temperature of the simulations, i.e., 390 K, is well in excess of the transition temperature.

How does one explain the observed concerted motion of the molecular layers in the phase transition involving DL-norleucine? The simulations suggest that this phenomenon must be energetically feasible. We therefore investigated the energy barriers for the shifting of an entire bilayer and that for the detachment of a single molecule from the edge of a bilayer into an adjacent vacancy defect. The potential energy surface for the bilayer shift, along with the corresponding accessible surface, is shown in Figure 4. The potential energy barrier for the bilayer shift $\Delta U^{\ddagger}_{\text{shift}}$ was estimated to be 2.9 kJ/mol *per molecule*. In comparison, the potential energy required to detach an individual molecule from the edge of a bilayer into a vacancy defect ΔU_{vac} within a field of surrounding molecules is about 30 kJ/mol. Following the often quoted argument (see, for example, reference 21) that the overall barrier to the shifting of a layer comprising n molecules will be $n\Delta G^{\ddagger}$ where $\Delta G^{\ddagger}$ is the activation energy for one molecule, one may infer that as n becomes large the barrier will become insurmountable, making concerted motion for any significant numbers of molecules impossible.

Clearly, the choice between molecule-per-molecule motion and concerted displacements involving large collections of molecules (or any other variation on this theme) must depend on the available pathways and the associated energy barriers. In this context, the available pathways will depend on the anisotropy of the forces characterizing the crystalline system and on the degree of perfection of the crystal, i.e., the density of defects including dislocations, point defects and vacancies. In not so perfect crystals, by virtue of the high density of defects, there is scope for the molecule-by-molecule mechanism. Consequently, for such crystals, interface advance would be expected to proceed along this pathway as it is characterized by a low-energy barrier. For more perfect crystals, the transformation can only be induced at high excess temperatures (defined as $\Delta T = |T_c - T|$, where T_c is the transition temperature). The implication is that, for such crystals, the low barrier (molecule-per-molecule) pathways are limited, and an increasing amount of thermal energy is required to open up other pathways that could include concerted molecular displacements. Indeed, this is exactly what experimental observations suggest: transformations in near-perfect crystals, being limited by nucleation require high excess temperatures and, when the transformation occurs, it occurs almost instantaneously over the entire crystal volume.[21]

The forces characterizing the DL-norleucine structures are strongly anisotropic. The structures comprise tightly bound bilayers (by virtue of hydrogen bonding) and weak van der Waals interactions between the bilayers. To move a single molecule from a lattice site into an adjacent vacancy requires the breaking of a number of hydrogen bonds. The required energy is significantly higher than the barrier that a molecule needs to overcome during layer displacement at the van der Waals surface, i.e., $\Delta U_{\text{vac}} > \Delta U^{\ddagger}_{\text{shift}}$. This disparity in the energy barriers characterizing the two proposed pathways is likely to favor entire bilayer displacements, the exception being highly disordered crystals at very low excess temperatures. A key characteristic of martensitic transformations is a specific crystal deformation that generates net motion or net force, which can only come from collective molecular displacements. The above considerations suggest that molecular displacements in martensitic transformations must follow a particular pathway (or a limited number of pathways) with a distinctly lower-energy barrier compared with other possibilities. A unique pathway would be consistent with the transformation exhibiting a specific orientational relationship between the parent and the daughter crystal phase, which is also a characteristic of martensitic transformations.

The above discussion considers wholesale movement of entire planes. An alternative, which is more likely, is that the transformation proceeds by the propagation of a localized displacement wave, akin to a kink or a wave in a carpet. In this scenario, the molecules need only overcome a *local barrier* that may be surmounted as result of thermal fluctuations but at lower excess temperatures. The essential basis of the soft-mode theory of displacive phase transformations is that the transformation occurs as a result of a particular lattice vibration, a normal mode (or phonon), whose frequency tends toward zero on transformation.[32,33] The molecular displacements associated with the specific normal mode are precisely those that result in the new phase. As the molecular displacements yielding the new phase occur, the restoring force against the displacements decays resulting in a drop in the frequency of the normal mode ("mode softening") or even its complete annihilation. Although a thorough investigation of the soft modes driving the DL-norleucine transformation is outside the scope of the present article, our observations reveal that the lattice vibrations along the *b*-axis (which is a common axis for both phases) appear to overcome the restoring force and drive the bilayers to their new relative positions that define the final structure. It might be tempting to consider that a molecule-by-molecule mechanism is not too dissimilar to the soft mode mechanism, being different only in terms of the coherence length, i.e., the number of molecules involved in the fluctuation traversing the structure. Normal modes are *collective* lattice vibrations. Furthermore, the diffusion rates in crystals, which are governed by vacancy defects, are significantly slower relative to lattice vibration frequencies.[34]

Finally, we comment on the effects of the technical variables, namely the barostat and thermostat coupling (relaxation) constants, τ_B and τ_T respectively, and the application or otherwise of bond constraints. The relaxation constants were investigated at two respective values, 1.0 and 10.0 ps for the barostat, and 0.1 and 1.0 ps for the thermostat. The larger barostat coupling constant $\tau_B = 10$ ps caused large and infrequent oscillations of the simulation box that appeared to perturb the continuous nature of the trajectory. This suggests that excessively large relaxation constants for the barostat should be avoided. The lower relaxation constant for the thermostat $\tau_T = 0.1$ ps (in combination with $\tau_B = 1.0$ ps) appeared to be ideal in that there was no marked build up of kinetic energy at any point during the transformation. In some molecular dynamics codes, the thermostat and barostat coupling is set in terms of an effective "mass" for the thermostat and barostat extended

(31) Devani, S.; Anwar, J. *J. Chem. Phys.* **1996**, *105*, 3215−3218.
(32) Cochran, W. *Ferroelectrics* **1981**, *35*, 3−8.
(33) Dove, M. T. *Amer. Mineral.* **1997**, *82*, 213−244.
(34) Shewman, P. *Diffusion in Solids*, 2nd ed; The Minerals, Metals and Materials Society: Warrendale, PA, 1988.

variables. The relaxation constants are related to the effective masses Q (thermostat) and W (barostat) by the relationships $Q = N_f k_B T_{Ext} \tau_T^2$ and $W = N_f k_B T_{Ext} \tau_B^2$, where N_f is the number of degrees of freedom of the system, k_B Boltzmann's constant, and T_{Ext} is the external (set) temperature.

In respect of the choice of constraining the molecular bonds or leaving them flexible, the common approach is to employ bond constraints that enable the use of a larger time step and hence giving access to longer timescales.[35] Our expectation was that flexible bonds, which will enable the molecule to be more accommodating, would reduce the activation energy barrier and enable the transformation to occur at a lower temperature and/or in a shorter simulation time. In our simulations, both systems (with and without bond constraints) transformed at the same temperature and in about the same simulation time, suggesting that the angle and torsional flexibility offered a sufficient degree of freedom.

In conclusion, we have carried out molecular dynamics simulations of a martensitic-type phase transformation in crystals of DL-norleucine, which reveal concerted molecular displacements involving entire bilayer shifts during the transformation. These observations can be rationalized on the basis that at sufficiently high excess temperatures the free energy barriers to concerted molecular displacements can be overcome by the available thermal energy. Furthermore, the molecular displacements exhibited in the DL-norleucine transformation can occur by the propagation of a displacement wave, which requires the molecules to overcome only a local barrier. We consider concerted molecular processes to be a dominant feature of interface advance in displacive transformations, particularly in near-perfect crystals. These findings are expected to be of value toward developing strategies for controlling or modulating martensitic-type transformations (in principle an individual molecular defect, e.g., an impurity, could disrupt concerted molecular displacements over a significant length scale) and, hence, realizing the potential of employing organic martensitic materials as tiny machines.

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Supporting Information Available: Snapshots from the trajectory of the crystal simulation with an entire row of vacancies. This material is available free of charge via the Internet at http://pubs.acs.org.

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(35) Ferrario, M.; Ryckaert, J. P. *Mol. Phys.* **1985**, *54*, 587−603.