Low-temperature orientational order and possible domain
structures in $C_{60}$ fullerite

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Abstract

Based on a simple model for ordering of hexagons on square planar lattice, an attempt has been made to consider possible structure of $C_{60}$ fullerite in its low temperature phase. It is shown that hexagons, imitating fullerenes oriented along $C_3$ axes of $sc$ lattice, can be ordered into an ideal structure with four non-equivalent molecules in unit cell. Then the energy degeneracy for each hexagon rotations by $\pi/3$ around its $C_3$ axis leaves the translational and orientational order in this structure, but leads to a random distribution of $\pi/3$ rotations and hence to “averaged” unit cell with two molecules. However the most relevant structural defects are not these intrinsic ”misorientations” but certain walls between the domains with different sequences of the above-mentioned two (non-ideal) sublattices. Numeric estimates have been made for the anisotropic inter-molecular potential showing that the anisotropy is noticeably smaller for molecules in walls than in domains.

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I. INTRODUCTION

Study of equilibrium thermodynamic properties of C\textsubscript{60} fullerite remains among actual topics in the low temperature physics. In particular, the recent experiments on its heat conduction \cite{1} and linear thermal expansion \cite{2} revealed the anomalies proper just to this unique object. This relates to the following properties observed in experiments.

i) Short enough (~50 intermolecular spacings) mean free path for acoustic phonons evidencing presence of a rather high amount (up to 10\%) of structural or impurity scatterers, despite only less then 10\textsuperscript{−2} wt.\% impurities are present in the initial material,

ii) Negative (and really huge, up to 10\textsuperscript{2} ) value of Grneisen coefficient in solid C\textsubscript{60} at $T \sim 10$K.

In particular, to explain the low temperature behavior of heat conductance in nominally pure C\textsubscript{60} fullerite, scattering processes of phonon heat carriers by some defects of orientational nature were invoked in Ref. \cite{1}. Namely, it was supposed that with cooling the crystal some single, ”orientationally disordered” C\textsubscript{60} molecules leave quenched in it. Then their relative number should reach several percents, or in other words, so many molecules become ”orientational impurities” that one of them can be found among nearest neighbors of each ”regular” molecule. This was justified by the estimates showing that if anisotropic part of inter-molecular interaction (AIMI) contains two minima with relatively small energy difference, but separated by a high enough ($\sim 3 \cdot 10^3$K) energy barrier, a considerable number of molecules can left frozen in the metastable state at $T \sim 10^2$ K and a reasonable cooling rate. However, estimates based on single-particle treatment considering relaxation of each molecule independent of others, at fixed (static) environment, hardly can be consistent. All the molecules are equivalent in the crystal, equally and self-consistently participating in formation of the crystalline (molecular) field on each of them, therefore the barriers should also depend on the relaxing molecules themselves. Subsequently, energy estimates for several particular orientations of a single molecule \cite{3} can hardly give a proper value of shortest
time of escape from its metastable state. At least, it should be noted that a great number of misoriented molecules can transform the crystal into an "orientational solution" or even into a glass (if this will be accompanied by unlimited extension of relaxation times spectrum). That idea of orientational glass and resulting competition between isotropic and anisotropic parts of intermolecular potential was proposed in Ref. [4] to explain the anomalous large negative thermal expansion of solid $C_{60}$ discovered by Aleksandrovskii et al. [2]. However, at present no numeric estimates are available for this mechanism that could confirm the observed expansion.

The above mentioned problems with justification of the proposed physics of anomalous thermal behavior of solid $C_{60}$ suggest one to seek some alternatives, more compatible with the translational invariance of a crystal. In this communication, one such mechanism is proposed, related to possible existence of several orientational domains in $sc$ phase of solid $C_{60}$, separated by well defined domain walls. The latter could play the role of effective scatterers for phonon heat carriers. Besides, the higher symmetry of local crystalline field on $C_{60}$ within the walls can restore the conditions for their almost free rotation, which is necessary (see Ref. [2] and references therein) to account for negative thermal expansion.

II. MODEL

It is well known (see, for example the reviews [3], [4]) that below the point of orientational melting $T_m^{(high)} \approx 260$ K the $fcc$ lattice of $C_{60}$ fullerite is divided into four $sc$ sublattices with one of the molecule $C_3$ axes oriented along one of the cube diagonals (which also are crystalline $C_3$ axes). It is of interest to notice that the corresponding $Pa\bar{3}$ structure, charac-

The collective character of crystalline modes should be also taken into account. A well-known example is vibrational or magnetic spectra resulting from single particle levels with excitation gap of the order of inter-particle interaction, which is considerably softened (down to Goldstone gapless behavior) after collectivization. Orientational modes are not exception in this sense.
teristic for simplest molecular cryocrystals where small quadrupole-quadrupole interactions dominate, permits to assume presence of an induced quadrupole moment on C$_{60}$ in fullerite, despite its complete absence for free C$_{60}$ molecule. Also it can be expected that no "transversal" order with respect to each of these axes takes place until the low temperature transition at $T_m^{(low)} \approx 90$ K. But since the molecules C$_{60}$ present truncated icosahedra, having 5th order axes among their symmetry elements, they cannot be completely ordered into $sc$ lattice by the impossibility of simultaneous optimization of local (crystal-field) and intermolecular potentials. Therefore certain kinds of defects are inevitable at low temperatures, either point (individual) or extended (collective).

The first type of defects is usually related to some local disturbance of structural or compositional order, while the second (as dislocations, domain walls, twin boundaries, etc.) can exist even at fully uniform background. Local disorder in fullerite could be due to, for example, isotopically substituted C$_{60}$ molecules, or C$_n$ fullerenes with $n \neq 60$, or impurities like H$_2$. But the samples of C$_{60}$ fullerite with the above-mentioned anomalies of low temperature properties were especially prepared and purified so that there were no physical reasons for any noticeable contents of local defects (including misoriented molecules).

Then a more plausible source of low temperature anomalies can be sought in extended (topological) defects, and in view of the possibility of several energetically equivalent domain

2Evidently, a number of thermal rotational excitations of C$_{60}$ molecules are present at $T > T_m^{(high)}$, all of them associated with certain multipole distortions. The lowest energies ($\sim 10^2$ cm$^{-1}$) relate to intra-molecular quadrupole vibrations, indistinguishable from rotations. Self-consistent admixture of these excitations into the molecule ground state in the crystal field reduces (below $T_m^{(high)}$) the almost spherical symmetry down to an axial, contributing to the total energy gain. So one can suppose that below $T_m^{(high)}$ the definite orientation of fullerenes along a $C_3$ axis is fixed and long-ranged, corresponding to the common order of quadrupoles. Otherwise, the $sc$ lattice cannot be realized.
structures to exist under reduced cubic symmetry, these defects can be associated with the walls between such domains.

Of course, even a simple cubic lattice made of so complex and symmetrical molecules as \( C_{60} \) presents great technical difficulties for straightforward calculation of full inter-molecular potential, defined by high-order multipole moments with great number of components, and of related low-energy (non-linear) excitations in the crystal. Hence, not pretending to give quantitative predictions for real fullerite, we limit ourselves below to consideration of a simplified model including the relevant features of fullerite: reduction of the crystalline point symmetry by its incompatibility with the molecular symmetry, a double-well potential of AIMI, and the related possibility for domains and domain walls.

Let us consider a system of flat hexagonal molecules (imitating \( C_{60} \) molecules seen along \( C_3 \) axis\(^3\)) located in sites of rigid square planar (\( sp \)) lattice, modeling 3D \( fcc \) lattice. To evaluate the angular part of pair interaction between electrically neutral hexagons, we suppose two kinds of negative charges, \(- (1 \pm \alpha)\), located at centers of hexagon sides and unit positive charges at their vertices (see Fig. 1a). Such distribution of negative charges recalls single covalent bonds at borders between pentagon and hexagon and double bonds between two hexagon rings in a truncated icosahedral molecule. Here the charge and geometric asymmetry parameter \( \alpha \), reducing the \( C_6 \) symmetry of a hexagon down to \( C_3 \), reflects one of the most important features of real \( C_{60} \) fullerene, 120\(^\circ\) alternation of such rings around each its hexagon.

The full Coulomb energy of a pair of hexagons (Fig. 1b) reads:

\[
V_{nm}(\theta_n, \theta_m) = \sum_{\mu, \sigma} V_{nm}^{(\mu \sigma)}(\theta_n, \theta_m),
\]

where the indices \( \mu, \sigma \) take the values \( v, b, \) or \( B \), related to vertices and to bonds with smaller and greater negative charges, respectively, and the particular terms are:

\(^3\)Since the same 3rd order rotational symmetry holds for fullerene molecules being projected at cube faces.
\[ V_{nm}^{(uv)}(\theta_n, \theta_m) = \sum_{j,k=0}^{5} \left\{ \left[ R_{nm} + \cos \left( \theta_n + \frac{\pi j}{3} \right) - \cos \left( \theta_m + \frac{\pi k}{3} \right) \right]^2 + 
\left[ \sin \left( \theta_n + \frac{\pi j}{3} \right) - \sin \left( \theta_m + \frac{\pi k}{3} \right) \right]^2 \right\}^{-1/2} , \] (2)

\[ V_{nm}^{(eb)}(\theta_n, \theta_m) = -(1 - \alpha) \sum_{j=0}^{5} \sum_{k=0}^{2} \left\{ \left[ R_{nm} + \cos \left( \theta_n + \frac{\pi j}{3} \right) - \right. \right. \\
\left. \frac{\sqrt{3}}{2} \cos \left( \theta_m + \pi \frac{4k+1}{6} \right) \right]^2 + \sin \left( \theta_n + \frac{\pi j}{3} \right) - \frac{\sqrt{3}}{2} \sin \left( \theta_m + \pi \frac{4k+1}{6} \right) \right\}^{-1/2} = \\
= V_{nm}^{(bb)}(\theta_n, \theta_m) = (1 - \alpha)^2 \sum_{j,k=0}^{2} \left\{ R_{nm} + \frac{\sqrt{3}}{2} \left[ \cos \left( \theta_n + \pi \frac{4j+1}{6} \right) - 
- \cos \left( \theta_m + \pi \frac{4k+1}{6} \right) \right]^2 + \frac{3}{4} \left[ \sin \left( \theta_n + \pi \frac{4j+1}{6} \right) - \sin \left( \theta_m + \pi \frac{4k+1}{6} \right) \right]^2 \right\}^{-1/2} = \\
= \frac{1 - \alpha}{1 + \alpha} V_{nm}^{(bb)}(\theta_n, \theta_m) = \frac{1 - \alpha}{1 + \alpha} V_{nm}^{(BB)}(-\theta_n, -\theta_m) = \left( \frac{1 - \alpha}{1 + \alpha} \right)^2 V_{nm}^{(BB)}(-\theta_n, -\theta_m) , \] (4)

\( R_{nm} = |n - m| \) is the distance between the centers of hexagons on the sites \( n \) and \( m \) of \( sp \) lattice; \( \theta_n, \theta_m \) are the relative orientation angles; the distance from center to vertex is unity. It can be noticed that, due to \( C_3 \) symmetry of charges in a hexagon, the clockwise and counterclockwise rotations are not equivalent in AIMI.

Despite the simplified geometry of \( sp \) lattice of hexagons and the neglecting of quantum effects (charge delocalization, covalency, etc.), one can expect this rather rough model to give a correct qualitative behavior of AIMI and its dependence on the charge distribution within the molecule and a reasonable estimate of contributions from different mutual configurations of molecules.
III. PAIR INTERACTIONS AND ORDERING TYPES

The numerical results for AIMI, Eq. 1, are shown in Fig. 2 for some typical mutual configurations and several values of the asymmetry parameter \( \alpha \). First of all, it is seen that, for \( \alpha \neq 0 \), AIMI for two hexagons possesses a distinct 120° periodicity and two-hump profiles. This reflects correctly AIMI for two \( C_{60} \) molecules where a double-well potential describes the so-called pentagon and hexagon configurations \( \text{(see also [5], [6])} \). It is also seen that with decreasing asymmetry of negative charge distribution, AIMI becomes smoother, though some minima (see Fig. 2a,b) become deeper, so that in the limit \( \alpha \to 0 \) all the minimum energies are equal and negative.

It follows from Fig. 2 that for all asymmetry values, except \( \alpha = 0 \), the most stable configuration is that where a vertex of one molecule points to a greater negative charge of neighbor molecule (Fig. 2a,c) while the maximum repulsion corresponds to parallel neighboring sides with such negative charges. At least, in the case \( \alpha = 0 \) the 60° periodicity corresponding to \( C_6 \) axis restored, nevertheless leaving the same (vertices against sides) most stable configuration.

Knowledge of pair interaction and most stable configurations for two hexagons enables one to order them in a \( sp \) lattice. Then AIMI requires that one of long axes of each hexagon be oriented along a crystalline axis and its nearest neighbors be rotated by \( \pi/6 \). This readily divides the \( sp \) lattice into two inter-twinned ones, with long hexagon axes aligned with \( x \) (”horizontal”, H) and \( y \) (”vertical”, V), respectively. But taking into account that a molecule has two non-equivalent positions with respect to negative charges for each alignment, the ideal order in \( sp \) lattice of such hexagons corresponds to ”parquets” (one of them is shown in Fig. 3) with four molecules in unit cell, two horizontal, denoted 1 and 3, and two vertical, 2 and 4. Then each of the two above-mentioned sublattices contains only even or odd positions. Here the long-range order holds not only for translations and orientations but also for the charge pattern. It should be also noted that, because of incompatible point groups for asymmetric hexagons and \( sp \) lattice, it is impossible to arrange all nearest neighbors of each
hexagonal molecule in positions with maximum negative AIMI. Though some its neighbors occur in metastable minima of AIMI, nevertheless the total energy balance proves to be negative and stable.

This kind of order is peculiar by its frustration, or the energy degeneracy with respect to the substitutions $1 \leftrightarrow 3$ and $2 \leftrightarrow 4$. These transformations are just generated by a $C_6$ rotation, which is not an element of symmetry group of a molecule with asymmetric charge distribution (see Fig. 1a). In its turn, this implies that the $sp$ lattice of hexagons, preserving the above described translational and orientational order can be created in a thermodynamical way with a specific disorder left within even and odd sites. This transforms the ideally ordered 4-sublattice into a non-ideal 2-sublattice structure like a simulated fragment shown in Fig. 4. In such a crystal the $C_6$ rotation intrinsically enters the point symmetry group of a molecule.

Evidently, 4- or 2-sublattice structures admit existence of several equivalent arrangements with permutated sublattices separated by certain extended defects, domain walls or anti-phase boundaries. These defects might effectively contribute into low temperature thermal properties of the system. Below we consider an example of such a defect in a 2-sublattice structure.

**IV. DOMAIN WALL STRUCTURE**

The above-indicated structure of 2-sublattice ordering of hexagons in $sp$ lattice provides equal conditions for all of them, and the mentioned disorder does not result in any characteristic isolated defects. This is also seen from Fig. 2 showing rather high barriers between

\footnote{Strictly speaking, the $C_6$-rotated molecule can change its distances to nearest neighbors, but we ignore this virtually small effect in view of average translational invariance of the lattice. At the same time, the AIMI analysis shows that the orientational order is not perturbed even under $C_6$ rotations.}
stable and metastable minima. Hence each hexagon, either in 4- or 2- sublattice structure stays near an AIMI minimum that defines its libration spectrum.

However this does not prevent defects at all in such a crystal. In particular, in the course of thermodynamical growth, there can appear, as usual, some vacancies and dislocations (which will not be discussed here) and also a specific kind of defects, the anti-phase boundaries, characteristic for any multi-sublattice orientational (vector or tensor) structure. They emerge between the regions, identical in their coordination but different in the attribution of molecule orientations to sublattices.

Actually, the transition from rotation to libration of molecules is a 1st kind transition, realized through formation of nuclei (domains) of orientational order with definite attribution of sublattices to molecule orientations. Extension of such domains (see Fig. 3) leads them to contact each other, forming a continuous ordered structure. There are two possible modes of such a "meeting". At the contacts ...HVHV→←HVHV... or ...VHVH→←VHVH... the two structures perfectly match, producing a single coherent domain. But the contacts ...VHVH→←HVHV... or ...HVHV→←VHVH... produce a mismatch, so that the closest molecules to the boundary should be orientationally tuned to provide a continuous transition from one domain to another. Evidently, far from the boundary such domains are indistinguishable and the boundary itself is just a consequence of the initial conditions of the growth. Moreover, no visible thermodynamical mechanisms for domain structure formation (like those known, for instance, in 2-sublattice antiferromagnets [10], [11]) can be indicated in this system of orientationally ordered hexagons.

To describe consistently the 2-sublattice structure, let us redefine the orientation angle \( \theta_{n,i} \) for an "averaged" molecule (possessing \( C_6 \) symmetry) at \( i \)th site in \( n \)th unit cell as the smallest positive angle between one of its vertices and \( y \)-axis (see Fig. 1b). Then for each unit cell we can naturally define the two angles

\[
\varphi_n = \theta_{n,2} - \theta_{n,1}, \quad \psi_n = \theta_{n,2} + \theta_{n,1},
\]

which play the role of order parameters. For the two fragments of ordered structures shown
in Fig. 5 the corresponding values are uniform in space: $\varphi_n = \varphi_I = \pi/6$, $\psi_n = \psi_I = \pi/6$ in the domain I, and $\varphi_n = \varphi_{II} = -\pi/6$, $\psi_n = \psi_{II} = \pi/6$ in the domain II. Thus the two domains are distinguished by the inversion of parameter $\varphi$, like $180^\circ$ domains in a 2-sublattice antiferromagnet.

One can build a boundary between these two domains, located at the origin and characterized by the unit normal vector $\mathbf{d}$, so that $\varphi_n$ changes when $\mathbf{n}$ crosses the domain wall, reaching asymptotic values $\varphi_n \to \varphi_I$ at $\xi = \mathbf{n} \cdot \mathbf{d} \to -\infty$, $\varphi_n \to \varphi_{II}$ at $\xi \to \infty$, and providing minimum to the energy functional:

$$E[\varphi_n, \psi_n] = \sum_n V_n (\varphi_n, \psi_n), \quad V_n (\varphi_n, \psi_n) = \sum_{\rho} V_{n,n+\rho} (\theta_n, \theta_{n+\rho}).$$

Using the above numerical simulation to estimate AIMI, we conclude that the function $V_n (\varphi_n, \psi_n)$ is well approximated by the sum of symmetric and antisymmetric parts:

$$V_n^{(s)} (\psi_n) + V_n^{(as)} (\varphi_n).$$

Then the antisymmetric part proves to be the softest mode so that the energy functional, Eq. (6) in continuous approximation, $\varphi_n \to \varphi (\xi)$, can be written as

$$E \left[ \varphi, \frac{\partial \varphi}{\partial \xi} \right] = \int_{-\infty}^{\infty} \left[ \frac{1}{2} a^2 v_1 \left( \frac{\partial \varphi}{\partial \xi} \right)^2 + \frac{1}{36} v_2 \cos 6\varphi \right].$$

In this approximation, the inhomogeneous re-orientations of hexagons across the domain boundary can be described by the sine-Gordon equation:

$$\frac{\partial^2 \varphi}{\partial \xi^2} + \frac{1}{3} d_{DW}^{-2} \sin 6\varphi = 0,$$

where the domain wall width $d_{DW} = a \sqrt{v_1/v_2}$ is of the order of lattice constant $a$. This is related to the fact that, unlike the common situation in magnets where as a rule $v_1$ (exchange, or stiffness constant) is much greater than $v_2$ (relativistic anisotropy), in the considered system both constants have the same origin in inter-molecular interactions and hence the same order of magnitude. Though, strictly speaking, Eq. (8) in this situation is only valid far enough from the domain boundary, orientations of discrete hexagons (obtained from a certain infinite discrete set of equations) will follow the “kink” solution $\varphi (\xi) = (1/3) \arcsin \tanh (\xi/2d_{DW})$ with sufficient accuracy. The factor $1/3$ here and in Eq. (8) provides a correct asymptotics.
for $\varphi(\xi)$: $\varphi(\pm \infty) = \pm \pi/6$. This also expresses the analogy of the $\pi/3$ rotation between the considered domains with the $\pi$ rotation between $180^\circ$ domains in ferro- and antiferromagnets.

Fig. 6 presents an example of a relatively narrow domain wall in the $sp$ lattice of hexagons. A sensible rotation of molecules with respect to their orientations in domains occurs within the stripe of $2 \div 3$ lattice parameters ($d_{DW} \sim a$), hence the misorientations are localized just in the domain wall. Notice that the 4-sublattice structure admits a richer systematics of domains (up to 4) and domain boundaries between them.

To examine how the dynamics of misoriented molecules differs from those in the domain, we estimated the antisymmetric part of AIMI, $V_{DW}^{(as)}(\varphi_{DW})$, for the closest unit cell to the center of domain wall. The corresponding potential relief shown in Fig. 7 is noticeably smoother and its minima, having the same $\pi/3$ periodicity, are much flatter than those for $V_{n}^{(as)}(\varphi_{n})$. Therefore the “orientational defects”, or molecules in domain wall, should display a softer libration spectrum with increasing density to lower energies. Besides, a specific low-energy excitation mode can appear, corresponding to oscillations of the antisymmetric order parameter $\varphi_{DW}$ which propagate along the wall (a ”bending” mode of orientational, not translational, origin).

The mentioned characteristics of a domain wall can be important for low-temperature behavior of the crystal. First of all, the collective defects should be stronger scatterers for thermal phonons than any point defects, especially if the phonon wavelength ($\lambda_T \sim h v_s/(k_B T)$, where the sound velocity $v_s \sim 3 \cdot 10^5\, \text{cm/s}$ [1]) becomes comparable with $d_{DW}$. Besides, a weaker AIMI in domain walls can permit the molecules there to remain almost free rotators down to much lower temperature than that of orientation freezing for the rest of the crystal.
V. CONCLUDING REMARKS

The presented consideration shows how peculiar can be dynamics of low-energy excitations in such a simple model system as that of hexagons on square lattice. In particular, for asymmetrical hexagons (possessing $C_3$ axis) this lattice turns out frustrated, which does not exclude a possibility for its glassy behavior. But even the frustrated lattice can be divided into two sublattices, leading to domain structure and domain walls. The latter, being of orientation origin, are able to effectively scatter the excitations of another origins, in particular, the phonons. However, the detailed analysis of such scattering goes beyond the scope of this work.

It seems that above results could be also relevant for fullerite. First of all, this relates to the possibility that $C_6$ rotation around fixed orientation of each $C_{60}$ molecule in the $sc$ phase could become effectively an element of the point symmetry group of the averaged crystal. Though the energy degeneracy conditioned by corresponding random "transverse" fullerene orientations also admits the existence of orientation glass state of fullerite, but the crystal as a whole remains uniform and no reasons can be found for any distinct point defects, including mis-orientations. However the extended topological defects, like orientation domain walls (which should not perturb initial attribution of $C_{60}$ molecules to cube diagonals), can exist even in a homogeneous system and provide an effective channel for dissipation of low energy quasi-particles.

Certainly, a more detailed theoretical study of these issues demands more realistic models, adequate to the fullerene and fullerite structures.

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FIG. 1. Charge distribution adopted for the model hexagon molecule (a) and possible orientations of two molecules with centers positioned at $n$ and $m$ (b).
FIG. 2. AIMI fo most characteristic (shown at left) mutual configurations of hexagons at fixed orientation of one of them. The axes and rotation angles correspond to Fig. 1b. The intermolecular distance $R_{12}$ was chosen 3 (in units of hexagon side).
FIG. 3. An example of ordering of hexagons into the $sp$ lattice with four molecules in unit cell and its translation vectors. Equivalent structures can be obtained by all permutations preserving opposite parities between nearest neighbors.
FIG. 4. Fragment of $sp$ lattice structure obtained by random substitutions $1 \leftrightarrow 3$ and $2 \leftrightarrow 4$ introduced into the ideal 4-sublattice structure in Fig. 3.
FIG. 5. A schematic of growths and approaching of two domains with orientationally ordered subsystems of hexagons. In the domain I (upper right) vertically oriented molecules (V, $\theta = 0$) are located in the sites of the 1st sublattice and horizontal (H, $\theta = \pi/6$) in 2nd sublattice, and in the domain II (lower left) the attribution is inverse.
FIG. 6. Domain wall (clear region) between two domains (dark regions, I and II of Fig. 5).

For convenience, the directors show the molecules orientations tilted with respect to the related asymptotics. The dashed line corresponds to the order parameter $\varphi = 0$. 
FIG. 7. Potential reliefs for the antisymmetric parts of AIMI in a domain and in the center of domain wall.