Structural models and electronic properties of icosahedral Al_6CuLi_3

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(Submitted July 5, 1993)
Zh. Eksp. Teor. Fiz. **104**, 4130–4142 (December 1993)

In this paper we discuss the problem of stability of quasicrystals, using the icosahedral crystal Al_6CuLi_3 as an example. We describe a method developed for calculating the structure and electronic properties of *sp*-quasicrystals on the basis of real decorated models. The general expression we obtain for the effective structure factor is convenient for practical applications and allows us to include certain (point) imperfections within the decorated Amman-Mackey model for both deterministic and randomized decorations. We have calculated the electronic properties of Al_6CuLi_3, based on the most likely structural model, within the weak-binding approximation, and found that the Fermi energy is located in the neighborhood of a local minimum of the electronic density of states.

Among the most intensely studied problems in the physics of quasicrystals is the stability of series of quasicrystalline phases. Many investigators are inclined to assume that quasicrystals are stable because the Fermi energy is located in a pseudogap (i.e., a local minimum in the electronic density of states[1–3]). Up to now, confirmation of this assertion has been sketchy, coming either from a hypothetical model of icosahedral aluminum[2] or from models that make use of crystalline analogs of such crystals.[3] In this paper we attempt to increase this information and to place conclusions regarding the stability mechanism of a quasicrystal and the large anomalies in its electronic properties on a more general footing. To this end we have developed a method for determining the structure of a quasicrystal with defects and calculating its electronic properties within the weak-binding approximation. We chose the stable icosahedral quasicrystal Al_6CuLi_3 as the object of our investigations.

This paper is constructed in the following way: in the first section various structural models of Al_6CuLi_3 are discussed; in the second the results of our calculations of the electronic properties of this quasicrystal are presented for the most probable structural model; and in the third part we present our conclusions.

1. DETERMINING THE STRUCTURE OF THE STABLE ICOSAHEDRAL QUASICRYSTAL Al_6CuLi_3

One approach to describing quasicrystalline structures is to use three-dimensional Penrose packing (otherwise referred to as the Amman–Mackey network) to determine exactly the atomic positions in three-dimensional space.[4,5] The elements of this packing are two types of rhombohedra—sharp and blunt. If we fill these rhombohedra with atoms, we obtain a decorated Penrose packing for which every position need not be occupied by an atom. The scale of the packing is characterized by the length of a rhombohedron a_R, which for this phase of Al_6CuLi_3 is approximately equal to 5.039 Å (Ref. 6). We can obtain the structure by using the projection method.[7] For a three-dimensional icosahedral quasicrystal we project from a six-dimensional space to the three-dimensional "physical" subspace. The projection bands that correspond to various decorated positions of the decorated Penrose packing "taper down" as the number of dimensions of the structural building blocks increases. It can be shown that the polyhedra described by projection bands for positions at vertices, edges, two-dimensional and three-dimensional facets of a six-dimensional hyperlattice are triakontahedra, rhombic icosahedra, rhombic dodecahedra, and rhombohedra (sharp or blunt), respectively.[8]

The expression for the structure factor in the case of decorated Penrose packing with randomly distributed structural vacancies is written as follows

$$S(\mathbf{q}_\parallel)=\sum_k \gamma_k \int_{(\infty)} \rho_k(\mathbf{r}_\parallel)\, e^{-i\mathbf{q}_\parallel \mathbf{r}_\parallel}\, d^3\mathbf{r}_\parallel\,, \qquad (1)$$

where

k is the type of "sublattice" of the decorated Amman–Mackey network (i.e., vertices, edges, faces, or positions within the rhombohedra);

γ_k is a renormalization coefficient for the contribution to the structure factor from each "sublattice" of the decorated Amman–Mackey network, arising from the presence of randomly distributed vacancies ($\gamma_k=1$ if there is no vacancy in the k-th sublattice, and $\gamma_k<1$ if there is);

ρ_k is the density of atoms in the kth "sublattice";

$\mathbf{q}_\parallel$ is a reciprocal lattice vector for the quasicrystal that corresponds to the "physical" parallel subspace;

$\mathbf{r}_\parallel$ is a vector in the direct lattice of the quasicrystal in the "physical" parallel subspace.

Noting that a point of type k in the six-dimensional space is present in the "physical" three-dimensional subspace only when the perpendicular component of its coordinate vector lies in the projection band described by a function of the form $n_k(\mathbf{r}_\perp - \mathbf{r}_{k_\perp})$, we can write

$$\rho_k(\mathbf{r}_\parallel)=\int_{(\infty)} \rho_k(\mathbf{r})\, n_k(\mathbf{r}_\perp - \mathbf{r}_{k_\perp})\, d^3\mathbf{r}_\perp\,, \qquad (2)$$

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where $\rho_k(\mathbf{r})$ is the density of atoms in the kth sublattice of the six-dimensional space; $\mathbf{r}_{k_\perp}$ is the perpendicular component of the basis radius vector for a position of type k in the six-dimensional hyperlattice.

Taking into account the orthogonality of the parallel and perpendicular subspaces along with (2), we are led to the following expression for $S^*(\mathbf{q}_\parallel)$ (the asterisk denotes complex conjugation)

$$S^*(\mathbf{q}_\parallel)=\frac{1}{(2\pi)^3}\sum_k \gamma_k \int_{(\infty)}\left\{\int_{(\infty)}\rho_k(\mathbf{r})e^{i\mathbf{qr}}d^6\mathbf{r}\right\} \times n_k(\mathbf{q}_\perp)e^{-i\mathbf{q}_\perp \mathbf{r}_{k_\perp}}d^3\mathbf{q}_\perp . \tag{3}$$

Equation (3) expresses the relation between the six-dimensional density of positions of type k and $S^*(\mathbf{q}_\parallel)$.

In order to introduce positional disorder caused by random displacements of atoms from their point positions in the six-dimensional hyperlattice into the structure, we will use the following representation of the modulated density:

$$\rho_k(\mathbf{r})_{\text{mod}}=\sum_t \delta(\mathbf{r}-\mathbf{r}_k-\mathbf{U}_k(\mathbf{t}+\mathbf{r}_k)-\mathbf{t}), \tag{4}$$

where t is a translation of the six-dimensional hyperlattice; $U_k(t+r_k)$ is the displacement for a position of type k in the six-dimensional space.

By using this representation of the modulated density, we bring out the fact that the projection band remains unchanged compared to the ideal case while the six-dimensional density is modulated. Then we can write

$$\int_{(\infty)}\rho_k(\mathbf{r})_{\text{mod}}e^{i\mathbf{qr}}d^6\mathbf{r} =\sum_t e^{i\mathbf{qr}_k}e^{i\mathbf{qt}}e^{i\mathbf{q}_\parallel \mathbf{U}_{k_\parallel}(\mathbf{t}+\mathbf{r}_k)}e^{i\mathbf{q}_\perp \mathbf{U}_{k_\perp}(\mathbf{t}+\mathbf{r}_k)}. \tag{5}$$

The parallel component of the displacement vector $\mathbf{U}_{k_\parallel}(\mathbf{t}+\mathbf{r}_k)$ corresponds to the usual phonon displacement in the "physical" subspace, while the perpendicular component $\mathbf{U}_{k_\perp}(\mathbf{t}+\mathbf{r}_k)$ is the phason displacement. The phonon displacement is small at room temperature, so that the scalar product $\mathbf{q}_\parallel U_{k_\parallel}(\mathbf{t}+\mathbf{r}_k)$ is small. Our estimates show that the primary contribution to the structure factor comes from vectors of the reciprocal lattice that have small components $Q_\perp$ (Ref. 9). Of course, the value of $\mathbf{q}_\perp U_{k_\perp}(\mathbf{t}+\mathbf{r}_k)$ could be small as well.

After expanding the exponential (5) in a series and averaging over the phason and phonon displacements, we find

$$\int \rho_k(\mathbf{r})e^{i\mathbf{qr}}d^6\mathbf{r}=e^{i\mathbf{qr}_k}e^{-1/2q_\parallel^2\,\overline{U^2_{k_\parallel},_{q_\parallel}}}e^{-1/2q_\parallel^2\,\overline{U^2_{k_\parallel},_{q_\parallel}}}\sum_{\mathbf{t}} e^{i\mathbf{qt}}. \tag{6}$$

According to the properties of lattice sums, we have

$$\sum_{\mathbf{t}} e^{i\mathbf{qt}}=\frac{(2\pi)^6}{a^6}\sum_{\mathbf{Q}}\delta(\mathbf{q}-\mathbf{Q}), \tag{7}$$

where a is the length of an edge of the six-dimensional hypercube; $\mathbf{q}$ is a vector of the six-dimensional reciprocal lattice; $\mathbf{Q}$ is a reciprocal lattice vector from the six-dimensional reciprocal lattice. Taking into account (6) and (7) we obtain

$$S^*(\mathbf{q}_\parallel)=\frac{(2\pi)^3}{a^6}\sum_{\mathbf{Q}}\delta(\mathbf{q}_\parallel-\mathbf{Q}_\parallel)S_u^*(\mathbf{Q}),$$

where

$$S_u^*(\mathbf{Q})=\sum_k \gamma_k \exp(i\mathbf{Q}_\parallel \mathbf{r}_{k_\parallel})\exp\left(-\frac{1}{2}\mathbf{Q}_\parallel^2\,\overline{U^2_{k_\parallel},_{\mathbf{Q}_\parallel}}\right) \times\exp\left(-\frac{1}{2}\mathbf{Q}_\perp^2\,\overline{U^2_{k_\perp},_{\mathbf{Q}_\perp}}\right) n_k(\mathbf{Q}_\perp);$$

here $\overline{U^2_{k_\parallel},_{\mathbf{Q}_\parallel}}$ and $\overline{U^2_{k_\perp},_{\mathbf{Q}_\perp}}$ are the mean-square projections of the displacements for atoms located in a sublattice of type k at $\mathbf{Q}_\parallel$ and $\mathbf{Q}_\perp$ respectively. It is clear that including the random displacements of atoms in the six-dimensional hyperlattice leads to the appearance of an additional phason Debye–Waller factor, analogous to the usual phonon Debye–Waller factor.

In general, we will assume the presence of site disorder in each of the "sublattices" of the Amman-Mackey network. If α_{mk} is the probability of observing an atom of type m in a sublattice of type k, then assuming the mean-square displacement projections for atoms of type m are the same for different k, we can write the effective structure factor for atoms of type m in the following way:

$$S_m^{\text{eff}}(\mathbf{q}_\parallel)=\frac{(2\pi)^3}{a^6}\exp\left(-\frac{1}{2}\mathbf{Q}_\parallel^2\,\overline{U^2_{m_\parallel},_{\mathbf{Q}_\parallel}}\right) \times\exp\left(-\frac{1}{2}\mathbf{Q}_\perp^2\,\overline{U^2_{m_\perp},_{\mathbf{Q}_\perp}}\right) \times\sum_{\mathbf{Q}}\sum_k \gamma_k\alpha_{mk}\delta(\mathbf{q}_\parallel-\mathbf{Q}_\parallel) \times[\exp(i\mathbf{Q}_\parallel \mathbf{r}_{k_\parallel})\ n_k(\mathbf{Q}_\perp)]^*. \tag{8}$$

Equation (8) contains the quantities $n_k(\mathbf{Q}_\perp)$, which are form factors (i.e., Fourier transforms of the shape functions) for the various types of positions ("sublattices"). These form factors may be calculated by summing the form factors for the displaced and mutually contacting rhombohedra that make up the polyhedra of the shape function for a given type of position ("sublattice"). It is not difficult to show that the form factor of a rhombohedron that "extends" along the edges $\mathbf{a}_{p_\perp}$, $\mathbf{a}_{j_\perp}$, and $\mathbf{a}_{k_\perp}$ and is displaced from the coordinate origin by $\mathbf{R}_{0_\perp}$ (at which point we locate the vertex of the rhombohedron) equals

$$n_{pjk}(\mathbf{Q}_\perp)=V_{pjk}e^{-i\mathbf{Q}_\perp \mathbf{R}_{0_\perp}}\prod_{l=p,j,k}\frac{1-e^{-i\mathbf{Q}_\perp \mathbf{a}_{l_\perp}}}{ie^{-i\mathbf{Q}_\perp \mathbf{a}_{l_\perp}}}. \tag{9}$$

There is special interest in the average atomic density of a decorated quasicrystal. It follows from the projection

TABLE I. Parameters for the deterministic decorated models of the structure Al_6CuLi_3. B—vertices of the rhombohedra; sr—middle of a rhombohedral edge, sg—facets of the rhombohedra, csr—centers of sharp rhombohedra.

Model	Atom	Decoration				Vacancy Concentration			
		B	sr	sg	csr	B	sr	sg	csr
1	Al	1	0	0	0	0	69	69	0
	Cu	0	0	0	1				
	Li	0	1	1	0				
2	Al	1	1	0	0	7	7	38	0
	Cu	0	0	0	1				
	Li	0	0	1	0				
3	Al	0	1	0	0	0	0	0	0
	Cu	0	0	0	1				
	Li	1	0	0	0				

formalism that the average atomic density for a position of type k (i.e., the number of points of type k per unit volume of the "physical" subspace) equals

$$\rho_k=\frac{p_kV_k}{a^6}, \tag{10}$$

where p_k is the number of polyhedra of type k that fit into an elementary unit cell of the six-dimensional hyperlattice; V_k is the volume of the polyhedron for the shape function of a "sublattice" of type k.

Since the average atomic density is an additive quantity, in general it equals

$$\rho_{NQ}=\frac{1}{a^6}\sum_k L_kp_kV_k, \tag{11}$$

where L_k is a decoration position of type k (0 or 1).

The weighted-mean density of the quasicrystal can easily be obtained from Eq. (11), i.e.,

$$\rho_{MQ}=\frac{1}{a^6}\sum_{k,m} L_kp_kV_k\alpha_{mk}M_m, \tag{12}$$

where M_m is the mass of an atom of type m.

All the decorations of the Amman–Mackey network can be conventionally divided into deterministic (with atoms of the same kind located within each sublattice of the Amman–Mackey network) and randomized (with atoms of different types located within each sublattice with various probabilities).

Three possible deterministic decorated models are shown in Table I. The first two models in Table I correspond to the stoichiometry of Al_6CuLi_3, while the third corresponds to that of $Al_{4.85}CuLi_{1.62}$, which is rather close to Al_6CuLi_3.

In calculating the randomized decorations of the Amman-Mackey network it is necessary to compute the quantities α_{mk}. Under the assumption of a definite stoichiometry and absence of vacancies in the "sublattices" of a decorated Amman-Mackey network, we can write the following systems of equations for α_{mk}:

$$\begin{cases} \sum\limits_k \rho_k\alpha_{mk}=c_m\sum\limits_k \rho_k, \\ \sum\limits_m \alpha_{mk}=1. \end{cases} \tag{13}$$

In Eq. (13) c_m is the atomic fraction of the components of the quasicrystal. For practical calculations it is necessary to add "bare" probabilities for a given type of atom to be located in each sublattice of the decorated Amman–Mackey network to system (13), which are chosen from crystal-chemical considerations. The most successful randomized decorated model is described in Table II. The calculated α_{mk} for this model were compared with the results of Ref. 6.

Of all the decorated models of Al_6CuLi_3 list here, only the randomized model gives satisfactory agreement with the experimental results.[10] The calculated diffraction spectrum of "polyquasicrystalline" Al_6CuLi_3 for Co radiation is shown in Fig. 1 for this model. It should be noted that we did not include the diffuse background in calculating the diffraction spectrum. The optimizations for the quantities $\overline{U^2_{m_\parallel}, \mathbf{Q}_\parallel}$ (Ref. 3) and $\overline{U^2_{m_\perp}, \mathbf{Q}_\perp}$ at room temperature are shown in Table III.

Table IV is made up of the experimental data from Ref. 11, which were obtained for single-crystal Al_6CuLi_3, and the results of the calculations in this paper for the randomized decorated Al_6CuLi_3 model. Based on these results the R-factor for agreement between the experimental and theoretical values of the structural amplitudes is found to be 0.09.

Computed electron diffraction patterns with fifth, third, and second order axes of symmetry are shown in Fig. 2 for the randomized decorated model of Al_6CuLi_3.

TABLE II. Parameters of a randomized decorated model of Al_6CuLi_3. The positions for the long diagonals of sharp rhombohedra are found by displacing a rhombohedron from its center along the long diagonal by a distance equal to $x=\pm 0.118034\cdot l_d$, where l_d is the length of the long diagonal of the sharp rhombohedron.

Atom	Probability of Location		
	vertices	Centers of Edges	Long Diagonals of Sharp Rhombohedra*
Al	0,69	0,75	0,17
Cu	0,22	0,10	0,00
Li	0,09	0,15	0,83

*The positions for the long diagonals of sharp rhombohedra are found by displacing a rhombohedron from its center along the long diagonal by a distance equal to $x=\pm 0.118034\cdot l_d$, where ld is the length of the long diagonal of the sharp rhombohedron.

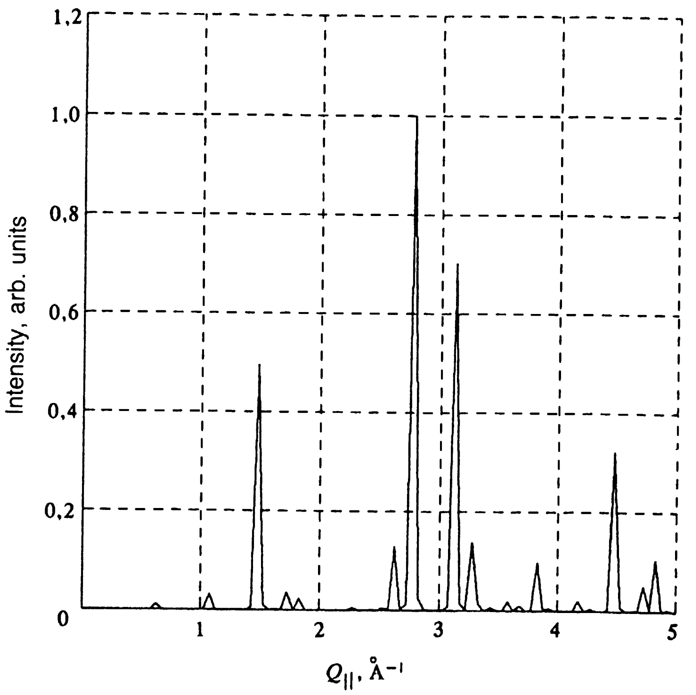

FIG. 1. Diffraction spectrum for Co radiation calculated for a randomized decorated model of poly-quasicrystalline Al_6CuLi_3, without structural vacancies. Broadening of the line is computed using a model with parameter equal to the diameter of a block D ($D=300$ Å).

For the randomized model adopted in this paper as a basis, calculations based on Eqs. (11) and (12) show that the average atomic density of Al_6CuLi_3 equals $5.55 \cdot 10^{22}$ atoms/cm^3, while the average weighted density is 2.56 g/cm^3. The experimental value of the average weighted density equals 2.40 g/cm^3 (Ref. 12). In view of the rather good agreement between the calculated and experimental diffraction spectra of Al_6CuLi_3, we can say that the value of the experimental average weighted density, which is smaller than the theoretical value, may indicate the presence of randomly distributed vacancies in the sublattices of the Amman–Mackey network. Among the possible reasons for generation of these vacancies is internal pressure, whose existence is easily demonstrated within the framework of a model of "hard spheres." An estimate of the average number of vacancies capable of explaining the experimental weighted-average density of Al_6CuLi_3 gives six unoccupied locations per 100 atomic positions.

TABLE III. Mean-square projection of phonon and phason displacements for various types of atoms.

Atom	$\overline{U^2}_{m_{\parallel},Q_{\parallel}}$, Å^2	$\overline{U^2}_{m_{\perp},Q_{\perp}}$, Å^2
Al	$1{,}267 \cdot 10^{-4}$	2,20
Cu	$5{,}256 \cdot 10^{-5}$	2,10
Li	$4{,}83 \cdot 10^{-4}$	2,10

2. CALCULATION OF THE ELECTRONIC PROPERTIES OF STABLE ICOSAHEDRAL QUASICRYSTAL Al_6CuLi_3

Since the components of the Al_6CuLi_3 phase are simple metals, we will use the method of pseudopotentials to calculate the electronic properties.

The Schroedinger equation for an electron in a quasicrystal can be written in the following form:

$$\left\{ -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r_{\parallel}^2} + V(\mathbf{r}_{\parallel}) \right\} \Psi(\mathbf{r}_{\parallel}) = \mu \Psi(\mathbf{r}_{\parallel}), \tag{14}$$

where m is the mass of an electron, $V(\mathbf{r}_{\parallel})$ is the quasiperiodic potential, $\Psi(\mathbf{r}_{\parallel})$ and μ are the eigenfunctions and eigenvalues of the operator

$$L(\mathbf{r}_{\parallel}) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial \mathbf{r}_{\parallel}^2} + V(\mathbf{r}_{\parallel}).$$

Let us carry out a factorization procedure for the quasicrystal. At the beginning we take the deterministic decorated model. Then

$$V(\mathbf{r}_{\parallel}) = \sum_{k} \sum_{w} v(\mathbf{r}_{\parallel} - \mathbf{R}_{wk_{\parallel}}), \tag{15}$$

where v is the pseudopotential of an individual ion, R_{wk} is the radius vector of the wth site in a "sublattice" of type k.

From (15) we can obtain after some uncomplicated transformations

TABLE IV. Experimental[11] and calculated values of the lengths of reciprocal lattice vectors **Q** and structural amplitudes $S(\mathbf{Q})$ for 14 reflections taken from the diffraction pattern obtained for single-crystal Al_6CuLi_3 (Mo radiation).*

Reflection Labels	Experiment		Calculations for the Randomized model	
	$Q, Å^{-1}$	$S(\mathbf{Q})$	$Q, Å^{-1}$	$S(\mathbf{Q})$
110000	1,059	0,0610	1,061	0,0609
111100	1,715	0,1020	1,716	0,1034
221001	2,775	0,8610	2,777	0,9956
332002	4,487	1,0000	4,493	1,0000
100000	0,626	0,0160	0,623	0,0349
111000	1,486	0,3030	1,486	0,4278
222100	3,145	0,6900	3,150	0,6855
332001	4,192	0,0620	4,199	0,0687
311111	3,260	0,2790	3,264	0,3152
422211	4,804	0,4050	4,810	0,3667
211100	2,268	0,0710	2,270	0,0425
211111	2,642	0,4940	2,641	0,4959
322101	3,828	0,3090	3,832	0,3311
333101	4,726	0,3080	4,733	0,2833

*When the atomic factors $f_m(\mathbf{Q}_\parallel)$ for the mth element are taken into consideration, the structural amplitude is $S'(\mathbf{Q}_\parallel)=\Sigma_m f_m(\mathbf{Q}_\parallel) S^{\text{eff}}(\mathbf{q}_\parallel)$.

$$V(\mathbf{q}_\parallel)=\frac{1}{\Omega}\sum_k S_k(\mathbf{q}_\parallel)\nu_k(\mathbf{q}_\parallel), \tag{16}$$

where Ω is the volume of the system, $S_k(\mathbf{q}_\parallel) = \Sigma_w e^{-i\mathbf{q}_\parallel \mathbf{R}_{wk_\parallel}}$ is the contribution to the structure factor from the kth "sublattice" of the decorated Amman–Mackey network, and

$$\nu_k(\mathbf{q}_\parallel)=\int d^3\mathbf{r}_\parallel\, \nu(\mathbf{r}_\parallel-\mathbf{R}_{wk_\parallel})e^{i\mathbf{q}_\parallel(\mathbf{R}_{wk_\parallel}-\mathbf{r}_\parallel)}$$

is the form factor of the pseudopotential of an ion located in the sublattice of type k. For the case of the randomized model, it is natural to replace $\nu_k(\mathbf{q}_\parallel)$ in Eq. (16) by the average of the form factors of the ionic pseudopotentials for ions located in a sublattice of type k, that is

$$\nu_k(\mathbf{q}_\parallel)=\sum_m \alpha_{mk}\nu_m(\mathbf{q}_\parallel). \tag{17}$$

Expression (17) implies that we have used the "virtual crystal" approximation in each of the sublattices.

Expression (16) can then be rewritten in the following fashion:

$$V(\mathbf{q}_\parallel)=\frac{1}{\Omega}\sum_m s_m^{\text{eff}}(\mathbf{q}_\parallel)\nu_m(\mathbf{q}_\parallel),$$

where $s_m^{\text{eff}}(\mathbf{q}_\parallel)$ is given by Eq. (8) when $\gamma_k=1$ for all k.

The expression for $s_m^{\text{eff}}(\mathbf{q}_\parallel)$ is conveniently rewritten in the form

$$s_m^{\text{eff}}(\mathbf{q}_\parallel)=\sum_{\mathbf{Q}}\delta(\mathbf{q}_\parallel-\mathbf{Q}_\parallel)F_m(\mathbf{Q}_\parallel), \tag{18}$$

where

$$F_m(\mathbf{Q}_\parallel)=\frac{(2\pi)^3}{a^6}\exp\left(-\frac{1}{2}\mathbf{Q}_\parallel^2\,\overline{U^2_{m_\parallel,\mathbf{Q}_\parallel}}\right)\times\exp\left(-\frac{1}{2}\mathbf{Q}_\perp^2\,\overline{U^2_{m_\perp,\mathbf{Q}_\perp}}\right)\times\sum_k \alpha_{mk}\cdot[\exp(i\mathbf{Q}_\parallel \mathbf{r}_{k_\parallel})\cdot n_k(\mathbf{Q}_\perp)]^*.$$

Let us introduce the operator $L(\mathbf{r})$:

$$L(\mathbf{r})=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial\mathbf{r}_\parallel^2}+U(\mathbf{r}), \tag{19}$$

where $U(\mathbf{r})$ is a periodic function in the six-dimensional space with Fourier transform

$$U(\mathbf{q})=\sum_{\mathbf{Q}}\left\{\frac{1}{\Omega}\sum_m F_m(\mathbf{Q}_\parallel)\nu_m(\mathbf{Q}_\parallel)\right\}\delta(\mathbf{q}-\mathbf{Q}). \tag{20}$$

Then we can write the following pseudo-Schroedinger equation in the six-dimensional space:

$$L(\mathbf{r})\Phi(\mathbf{r})=E\Phi(\mathbf{r}), \tag{21}$$

where $\Phi(\mathbf{r})$ are eigenfunctions and E the eigenvalues of the operator $L(\mathbf{r})$. It is easy to show that the dispersion laws for $\mu(\mathbf{k}_\parallel)$ and $E(\mathbf{k})$ are connected by the following relation:[13]

$$\mu(\mathbf{k}_\parallel)=E(\mathbf{k}_\parallel). \tag{22}$$

Therefore, in order to find the dispersion law for the quasicrystal it is sufficient to solve the pseudo-Schroedinger equation (21).

Making use of the standard procedures, in the approximation of weakly coupled electrons we find in second-order perturbation theory that

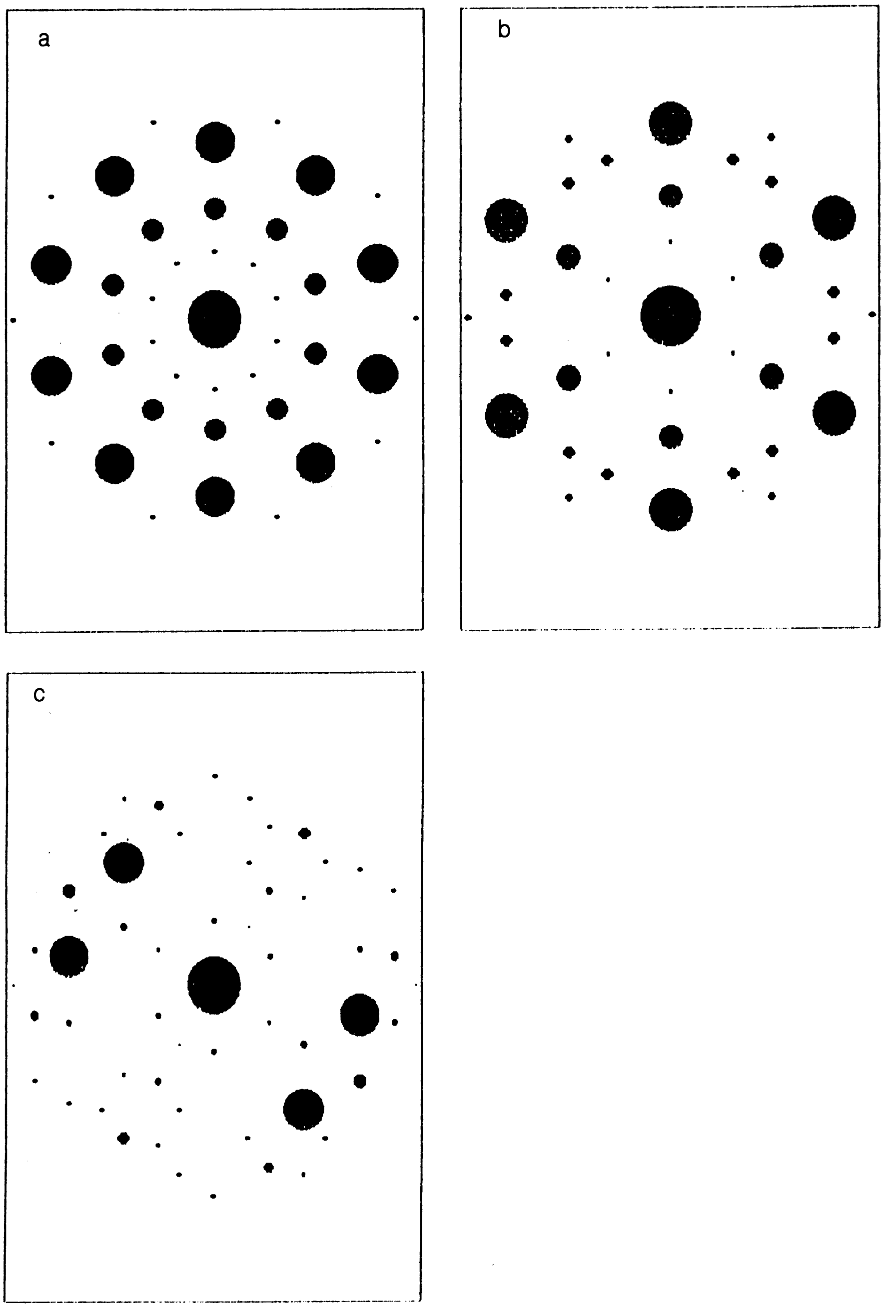

FIG. 2. Electron diffraction pattern for a randomized decorated model of a single quasicrystal of Al_6CuLi_3, which indicates the presence of (a) fifth-order symmetry axes, (b) third-order symmetry axes, and (c) second-order symmetry axes. The areas of the circles are proportional to scattering intensities.

$$\mu(\mathbf{k}_\parallel)=\varepsilon(\mathbf{k}_\parallel)^0+\frac{1}{\Omega}\left|\sum_m F_m(0)\nu_m(0)\right| + \sum_{\mathbf{Q}\neq0}\frac{\left|\frac{1}{\Omega}\Sigma_m F_m(\mathbf{Q}_\parallel)\nu_m(\mathbf{Q}_\parallel)\right|^2}{\varepsilon(\mathbf{k}_\parallel)^0-\varepsilon(\mathbf{k}_\parallel-\mathbf{Q}_\parallel)^0},$$

where

$$\varepsilon(\mathbf{k}_\parallel)^0=\frac{\hbar^2\mathbf{k}_\parallel^2}{2m}.$$

Near the Bragg planes (for which $|\mathbf{k}_\parallel|=|\mathbf{k}_\parallel-\mathbf{Q}_\parallel|$) it is necessary to use degenerate perturbation theory. For this case we may write

$$\mu(\mathbf{k}_\parallel)=\varepsilon(\mathbf{k}_\parallel)^0+\frac{1}{\Omega}\left|\sum F_m(0)\nu_m(0)\right| \pm\frac{1}{\Omega}\left|\sum F_m(\mathbf{Q}_\parallel)\nu_m(\mathbf{Q}_\parallel)\right|. \tag{23}$$

Although we are not allowed to introduce a Brillouin zone in quasicrystals, the concept of a pseudo-Brillouin zone, which is responsible for the presence of singularities in the electronic properties of a quasicrystal, is widely used in the literature. In this paper, in view of the large repetition factor for vectors of the reciprocal lattice of the quasicrystal, we will choose the pseudo-Brillouin zone to be spherical.

Within the framework of these approximations, the following picture of the dispersion law and density of electronic states emerges. At points of osculation of the Fermi sphere with the spherical pseudo-Brillouin zone we will observe an energy gap in the dispersion curve $E(\mathbf{k}_\parallel)$, in accordance with (23). Consequently, we will have a series of Van Hove singularities in the electronic density of states $N(E)$, connected with each vector of the reciprocal lattice of the quasicrystal.

Let us divide the density of electronic states into two components: a regular component $N_{\text{reg}}(E)$ and a singular part $N_{\text{sing}}(E)$. For $N_{\text{reg}}(E)$ it is natural to use the free-electron approximation. For $N_{\text{sing}}(E)$, according to Ref. 14, we can write

$$N_{\text{sing}}(E)=p_{\mathbf{Q}_\parallel} 2b \frac{1}{E_c} \{(\alpha^2-v^2)^{1/2} \operatorname{sgn} \alpha \theta(\alpha^2-v^2)-\alpha\}, \tag{24}$$

where $p_{\mathbf{Q}_\parallel}$ is the repetition factor for the reciprocal lattice vector $\mathbf{Q}_\parallel$;

$$b=(1/16\pi^2)\Omega_a\{\hbar\mathbf{Q}_\parallel/2\}^3$$

is a dimensionless factor, which contains the average atomic volume Ω_a for the phase under discussion; $\alpha=[E-E_c]/E_c$ is the degree of closeness of the Fermi sphere to the pseudo-Brillouin zone, where $E_c=(\hbar^2\mathbf{Q}_\parallel^2/8m)$;

$$v=|V(\mathbf{Q}_\parallel)|/E_c.$$

The computed curve for the density of electronic states $N(E)$, which takes into account the influence of the 251 strongest diffraction peaks, is shown in Fig. 3 for a randomized model of Al_6CuLi_3 without vacancies. In calculating $V(\mathbf{Q}_\parallel)$ for aluminum and lithium we used the Heine-Abarenkov pseudopotential model, while for copper we carried out a cubic spline interpolation of the data given by Moriarty.[15]

Estimates of the Fermi energy E_F under the assumption that the mean valence of Al_6CuLi_3 equals 2.2 for the randomized model without vacancies gives a value of 0.753 Ry (the free-electron model gives a Fermi energy of 0.716 Ry). Including the vacancies decreases the Fermi energy to a value of 0.745 Ry. The estimated values of the Fermi energy of Al_6CuLi_3 are located in the neighborhood of a local minimum of the density of states, that is, in a pseudogap. Therefore, we may say that the stability of the icosahedral quasicrystal Al_6CuLi_3 is conveniently described by the Hume–Rothery criterion, which has been repeatedly pointed out in the past.[3,16] The discrepancy between the positions of E_F and the pseudogap may be the cause of metastability of the quasicrystals. According to our calculations, the set of vectors of the reciprocal lattice with labels (311111) are responsible for the appearance of a pseudogap at the Fermi level of Al_6CuLi_3 (using Elser's labeling scheme[9]), although the set (222100) gives rise to a very deep local minimum in the density of states. This result confirms the conclusions of Karlsson[17] and attests to the importance of the shell of vectors (311111) for Al_6CuLi_3.

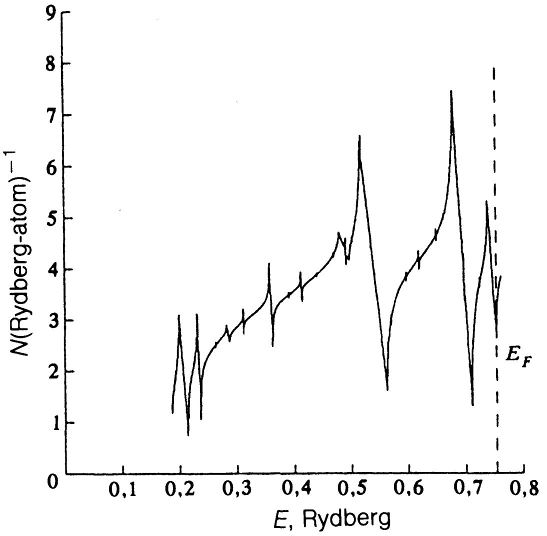

FIG. 3. Density of electronic states for the randomized decorated model of Al_6CuLi_3 without vacancies. The position of the Fermi energy is indicated by the dashed curves.

3. CONCLUSIONS

In this paper we have obtained a general analytic expression for the structure factor of a decorated icosahedral quasicrystal, including the presence of randomly distributed vacancies in sublattices of the Amman–Mackey network as well as phason and phonon Debye–Waller factors. We have made a selection of the various decorated models and have calculated the corresponding electronic properties for the stable icosahedral quasicrystal Al_6CuLi_3. We have shown that the structure of Al_6CuLi_3 is best described by a randomized model with a large fraction of structural vacancies (on the order of 6 atomic percent). Within the framework of the pseudopotential method and the approximation of a spherical pseudo-Brillouin zone we have calculated the density of electronic states and estimated the Fermi energy E_F for the most probable randomized structural model. This allows us to state our conclusions about the stability mechanism of Al_6CuLi_3 with more conviction than in the previous works.[2,3] The randomized model of Al_6CuLi_3 without structural vacancies leads to a position of E_F at a local minimum of the density of electronic states which is due to the reciprocal lattice vector with labels (311111). The inclusion of vacancies lowers the value of E_F somewhat; nevertheless, E_F remains in the pseudogap caused by this set of vectors. Therefore, we may assert that, first of all, the stability of the icosahedral quasicrystal Al_6CuLi_3 is satisfactorily described by the Hume–Rothery criterion; and, secondly, the shell of vectors (311111) is responsible for the pseudogap at the Fermi level, and not (222100) as was assumed previously (see, e.g., Refs. 3, 16).

It should be noted that the number of structural vacancies we have obtained, which leads to a contribution on the order of 10 $\mu\Omega\cdot$cm (293 K) to the specific resistance of Al_6CuLi_3, cannot explain the large value of this quantity [on the order of 800 $\mu\Omega\cdot$cm for 270 K (Ref. 12)].

The authors are grateful to A. V. Ruban for his attention to the work and useful discussions.

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Translated by Frank J. Crowne