Electrostatic energy of a multicomponent icosahedral quasicrystal with a basis in the case of a substitutional disorder

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A study is made of the effect of a substitutional disorder on the electrostatic energy of a multicomponent icosahedral quasicrystal whose structure is a decorated Amman–McKay network. In the absence of a short-range order, taking an average of fluctuations of the ion charges leads to an average valence in the final expression for the electrostatic energy. The general analytic expression derived here is convenient for finding the Madelung constant of decorated Amman–McKay networks. © *1994 American Institute of Physics.*

An important problem in the physics of quasicrystals is to identify the reasons for the stability of quasiperiodic phases. One approach to the solution of this problem is to calculate the binding energies of quasicrystal structures, which are dominated by the electrostatic energy and the band energy. Smith and Ashcroft have calculated the electrostatic energy of a one-component icosahedral quasicrystal with a structure based on a primitive (undecorated) Amman–McKay network, found as the result of a "paving" of the space with two types of rhombohedra: acute and obtuse, with atoms at their vertices.[1,2] However, the structures of real quasicrystals are described poorly by this model, and calculating the electrostatic energy of multicomponent quasiperiodic phases is not a trivial matter. A more general structural model of a real icosahedral quasiperiodic is a decorated Amman–McKay network with a substitutional disorder within the various "sublattices" (the atoms of the different species can lie not only at vertices of the rhombohedra but also on their edges, on their faces, and in their "interiors"; each set of these positions is characterized by a substitutional disorder).[3] A substitutional disorder for a crystalline configuration does not, as we know, give rise to an additional component of the electrostatic energy, and the average valence of the ions figures in the final expression.[4] The "sparseness" of the reciprocal lattice of a crystal was utilized to find this result in Ref. 4, because of an incorrect averaging of charge fluctuations. Actually, the reciprocal lattice of an icosahedral quasicrystal is dense everywhere,[5] so the formal use of the approach of Ref. 4 may lead to incorrect results. Our purpose in the present letter is to examine the effect of a substitutional disorder on the electrostatic energy of an icosahedral quasicrystal, taking account of particular structural features of the reciprocal lattice of a decorated Amman–McKay network, along with an estimate of the Madelung constant α_M for several structural models of an icosahedral quasicrystal. The latter approach leads to a more reliable conclusion regarding the role played by the band energy in the problem of the stability of an icosahedral quasicrystal.

For simplicity we consider a decorated Amman–McKay network at whose vertices there are ions of two species, A and B, which are "immersed" in a negatively charged uniform electron background. The structure-dependent part of the electrostatic energy is given by

$$E^s=\frac{e^2}{2N}\sum_{R_\parallel,R'_\parallel}{}' \frac{[C_{\mathbf{R}_\parallel}Z_A+(1-C_{\mathbf{R}_\parallel})Z_B][C_{\mathbf{R}'_\parallel}Z_A+(1-C_{\mathbf{R}'_\parallel})Z_B]}{|\mathbf{R}_\parallel-\mathbf{R}'_\parallel|}, \tag{1}$$

where N is the number of ions in the quasicrystal, $C_{\mathbf{R}_\parallel}$ are occupation numbers ($C_{\mathbf{R}_\parallel}=1$ if there is an ion of species A at the vertex with radius vector $\mathbf{R}_\parallel$; $C_{\mathbf{R}_\parallel}=0$ is there is an ion of species B there), and Z_A and Z_B are the valences of ions A and B, respectively.

Formally, we can rewrite expression (1) as follows:

$$E^s=\frac{e^2}{2N}\sum_{\mathbf{R}_\parallel,\mathbf{R}'_\parallel}{}' \frac{[C_{\mathbf{R}_\parallel}Z_A+(1-C_{\mathbf{R}_\parallel})Z_B][C_{\mathbf{R}'_\parallel}Z_A+(1-C_{\mathbf{R}'_\parallel})Z_B]}{|\mathbf{R}_\parallel-\mathbf{R}'_\parallel|}$$

$$\times\operatorname{erfc}(\eta^{1/2}|\mathbf{R}_\parallel-\mathbf{R}'_\parallel|)+\frac{e^2}{2}\int_{(\infty)}d^3\mathbf{r}_\parallel g(\mathbf{r}_\parallel)P(\mathbf{r}_\parallel), \tag{2}$$

where η is the Ewald parameter,

$$g(\mathbf{r}_\parallel)=\frac{\operatorname{erf}(\eta^{1/2}|\mathbf{r}_\parallel|)}{|\mathbf{r}_\parallel|},$$

$$P(\mathbf{r}_\parallel)=\frac{1}{N}\sum_{\mathbf{R}_\parallel,\mathbf{R}'_\parallel}[C_{\mathbf{R}_\parallel}Z_A+(1-C_{\mathbf{R}_\parallel})Z_B][C_{\mathbf{R}'_\parallel}Z_A+(1-C_{\mathbf{R}'_\parallel})Z_B]$$

$$\times\delta[\mathbf{r}_\parallel-(\mathbf{R}_\parallel-\mathbf{R}'_\parallel)]-[CZ_A^2+(1-C)Z_B^2]\delta(\mathbf{r}_\parallel),$$

and C is the concentration of the A ions.

After a Poisson transformation, the second term in (2) becomes

$$\frac{e^2}{2(2\pi)^3}\int_{(\infty)}d^3\mathbf{q}_\parallel g(\mathbf{q}_\parallel)P(-\mathbf{q}_\parallel).$$

Evaluating the corresponding Fourier transforms, we can write

$$E^s=\frac{e^2}{2N}\sum_{\mathbf{R}_\parallel,\mathbf{R}'_\parallel}{}' \frac{[C_{\mathbf{R}_\parallel}Z_A+(1-C_{\mathbf{R}_\parallel})Z_B][C_{\mathbf{R}'_\parallel}Z_A+(1-C_{\mathbf{R}'_\parallel})Z_B]}{|\mathbf{R}_\parallel-\mathbf{R}'_\parallel|}\cdot$$

$$\times\operatorname{erfc}(\eta^{1/2}|\mathbf{R}_\parallel-\mathbf{R}'_\parallel|)+\frac{e^2N}{4\pi^2}\int_{(\infty)}d^3\mathbf{q}_\parallel\frac{\exp\left(-\frac{\mathbf{q}_\parallel^2}{4\eta}\right)}{\mathbf{q}_\parallel^2},$$

$$\times|Z_BS(\mathbf{q}_\parallel)+(Z_A-Z_B)C_{\mathbf{q}_\parallel}|^2-e^2\overline{Z^2}\left(\frac{\eta}{\pi}\right)^{1/2}, \tag{3}$$

where

$$S(\mathbf{q}_\parallel)=\frac{1}{N}\sum_{\mathbf{R}_\parallel}\exp(i\mathbf{q}_\parallel\mathbf{R}_\parallel),\quad C\mathbf{q}_\parallel=\frac{1}{N}\sum_{\mathbf{R}_\parallel}D_{\mathbf{R}_\parallel}\exp(i\mathbf{q}_\parallel\mathbf{R}_\parallel),$$

$$\overline{Z^2}=CZ_{\mathrm{A}}^2+(1-C)Z_{\mathrm{B}}^2.$$

Taking an average of (3) over occupation numbers, we find, in the absence of a short-range order,

$$\overline{C_{\mathbf{R}_\parallel}C_{\mathbf{R}'_\parallel}}=C^2+\delta_{\mathbf{R}_\parallel,\mathbf{R}'_\parallel}(C-C^2),$$

$$\overline{C_{\mathbf{q}_\parallel}}=CS(\mathbf{q}_\parallel),$$

$$\overline{C_{\mathbf{R}_\parallel}C^*_{\mathbf{q}_\parallel}}=C^2|S(\mathbf{q}_\parallel)|^2+\frac{1}{N}C(1-C).$$

We then find

$$E^s=\frac{e^2}{2N}(\bar{Z})^2\sum_{\mathbf{R}_\parallel,\mathbf{R}'_\parallel}{}'\frac{\mathrm{erfc}(\eta^{1/2}|\mathbf{R}_\parallel-\mathbf{R}'_\parallel|)}{|\mathbf{R}_\parallel-\mathbf{R}'_\parallel|}+\frac{e^2N}{4\pi^2}(\bar{Z})^2$$

$$\times\int_{(\infty)}d^3\mathbf{q}_\parallel\frac{\exp\left(-\frac{\mathbf{q}_\parallel^2}{4\eta}\right)}{\mathbf{q}_\parallel^2}|S(\mathbf{q}_\parallel)|^2+e^2(Z_{\mathrm{A}}-Z_{\mathrm{B}})^2C(1-C)\left(\frac{\eta}{\pi}\right)^{1/2}-e^2\overline{Z^2}(\eta/\pi)^{1/2},\tag{4}$$

where $\bar{Z}=CZ_{\mathrm{A}}+(1-C)Z_{\mathrm{B}}$.

It can be shown[3] that, for an infinite ($N\rightarrow\infty$) icosahedral quasicrystal with a basis

$$S(\mathbf{q}_\parallel)=\frac{\rho(\mathbf{q}_\parallel)}{\rho(0)}=\frac{1}{\rho(0)}\frac{(2\pi)^3}{a^6}\sum_{\mathbf{Q}}\delta(\mathbf{q}_\parallel-\mathbf{Q}_\parallel)G_u(\mathbf{Q}),$$

where $\rho(\mathbf{q}_\parallel)$ is a Fourier transform of the density of the icosahedral quasicrystal, and a is the lattice constant of the six-dimensional hyperlattice, from which a projection is made for the purpose of obtaining the decorated Amman–McKay network, we have

$$G_u(\mathbf{Q})=\sum_k\exp[i\mathbf{Q}_\parallel\mathbf{r}_{k_\parallel}]n_k(\mathbf{Q}_\perp),$$

Here k is the index of the "sublattice" of the decorated Amman–McKay network, $\mathbf{Q}_\parallel$ and $\mathbf{Q}_\perp$ are the parallel and perpendicular components of the reciprocal-lattice vector $\mathbf{Q}$ of the 6D crystal, $\mathbf{r}_{k_\parallel}$ is the parallel component of the radius vector of the basis of the 6D hyperlattice, and $n_k(\mathbf{Q}_\perp)$ is a weight factor—the Fourier transform of the form function for the kth sublattice of the decorated Amman–McKay network.[3]

Expression (4) then becomes

$$E^s=\tfrac{1}{2}(\bar{Z})^2e^2\left\{\frac{1}{N}\sum_{\mathbf{R}_\parallel\mathbf{R}'_\parallel}{}' \frac{\operatorname{cerfc}(\eta^{1/2}|\mathbf{R}_\parallel-\mathbf{R}'_\parallel|)}{|\mathbf{R}_\parallel-\mathbf{R}'_\parallel|}\right.$$

$$\left.+\frac{4\pi}{v_0}\sum_{\mathbf{Q}}\frac{\exp\left(-\frac{\mathbf{Q}_\parallel^2}{4\eta}\right)}{\mathbf{Q}_\parallel^2}|L(\mathbf{Q})|^2-2\left(\frac{\eta}{\pi}\right)^{1/2}\right\}, \qquad (5)$$

where v_0 is the average volume per ion $[v_0=(a^6/\Sigma_k V_k N_k)]$,

$$L(\mathbf{Q})=\frac{G_u(\mathbf{Q})}{\Sigma_k V_k N_k},$$

V_k is the volume of the shape-function polyhedron for the kth sublattice of the decorated Amman–McKay network, and N_k is the decoration of the kth sublattice ($N_k=1$ if the kth sublattice is occupied; $N_k=0$ if it is vacant).

After the standard procedure of incorporating the structure-independent contributions to the electrostatic energy, we find

$$E^s=\tfrac{1}{2}(\bar{Z})^2e^2\left\{\frac{1}{N}\sum_{\mathbf{R}_\parallel\mathbf{R}'_\parallel}{}' \frac{\operatorname{cerfc}(\eta^{1/2}|\mathbf{R}_\parallel-\mathbf{R}'_\parallel|)}{|\mathbf{R}_\parallel-\mathbf{R}'_\parallel|}\right.$$

$$\left.+\frac{4\pi}{v_0}\sum_{\mathbf{Q}}{}'\frac{\exp\left(-\frac{\mathbf{Q}_\parallel^2}{4\eta}\right)}{\mathbf{Q}_\parallel^2}|L(\mathbf{Q})|^2-\frac{\pi}{\eta v_0}-2\left(\frac{\eta}{\pi}\right)^{1/2}\right\}. \qquad (6)$$

Again using the approximation which we used in going from (4) to (5), we can put the latter expression in the form

$$E^s=\tfrac{1}{2}(\bar{Z})^2e^2\left\{\sum_{|\mathbf{R}_\parallel|}{}' n_{|\mathbf{R}_\parallel|}\frac{\operatorname{cerfc}(\eta^{1/2}|\mathbf{R}_\parallel|)}{|\mathbf{R}_\parallel|}+\frac{4\pi}{v_0}\sum_{\mathbf{Q}}{}'\frac{\exp\left(-\frac{\mathbf{Q}_\parallel^2}{4\eta}\right)}{\mathbf{Q}_\parallel^2}|L(\mathbf{Q})|^2\right.$$

$$\left.-\frac{\pi}{\eta v_0}-2\left(\frac{\eta}{\pi}\right)^{1/2}\right\}, \qquad (7)$$

where $n_{|\mathbf{R}_\parallel|}$ is the frequency at which vectors of a given length $|\mathbf{R}_\parallel|$ are "meetable" in a decorated Amman–McKay network:

$$n_{|\mathbf{R}_\parallel|}=\lim_{N\to\infty}\frac{N_{|\mathbf{R}_\parallel|}}{N},$$

where $N_{|\mathbf{R}_\parallel|}$ is the number of vectors of length $|\mathbf{R}_\parallel|$.

It can be seen from expression (7) that in the case of a substitutional disorder, for the quasiperiodic structure under consideration here, we find an expression for the electrostatic energy which is similar to the Ewald expression, which includes an average valence of the ions. This result applies to both crystalline and quasicrystalline structures, regardless of how "sparse" the reciprocal lattice is. This approach covers a fairly wide range of icosahedral models based on the decoration of Amman–McKay networks, the only exceptions being models which have a short-range order within quasicrystal configurations.

The analytic expression derived for E_{es} can be used to calculate the electrostatic energy of any quasicrystal configuration with a substitutional disorder. This expression can easily be generalized to the case of a quasiperiodic structure with a substitutional disorder within the different sublattices of the decorated Amman–McKay network. It can also be used to calculate Madelung constants for various quasilattices. As an example we will estimate the Madelung constant for three quasicrystal structures (for estimates of $n_{|\mathbf{R}_{\|}|}$ we use a fragment of an Amman–McKay network consisting of 6291 atoms at the vertices of rhombohedra): $\alpha_M^{\text{v}}=1.66$ (the vertices of the rhombohedra of the network are occupied), $\alpha_M^{\text{e}}=1.56$ (the middles of the edges of the rhombohedra of the network are occupied), and $\alpha_M^{\text{ve}}=1.55$ (both the vertices and the middles of the edges of the rhombohedral of the network are occupied). The Madelung constant of these quasilattices is considerably lower than those of typical close-packed crystal structures ($\alpha_M\sim 1.79$). This circumstance, which can be assumed to be a general property of decorated Amman–McKay networks, evidently indicates that the band energy plays an important role in their stability.

The approach taken in this letter can also be taken for quasicrystals with a symmetry other than icosahedral.

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