Electronic structure of Al$_6$Mg$_4$Cu quasicrystals

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Abstract. The electronic structure of Al$_6$Mg$_4$Cu quasicrystal has been calculated by two methods, i.e. self-consistent recursion method (RM) in real space and ab initio molecular dynamics (AIMD) in reciprocal space. The last one is more modern and powerful. The realistic atomic-structure model of the quasicrystal has been used in both cases (QCIC model). The electronic total density of states (TDOS) with pseudo gap on the Fermi level has been obtained both in RM and AIMD calculations. The atomic structure relaxation has been needed in second case for obtain good TDOS with pseudo gap on Fermi level. The partial density of states (PDOS) has been use for analyse electronic structure of Al$_6$Mg$_4$Cu quasicrystal. The spiky states has been observed in real space and has not been observed in reciprocal space.

1. Introduction

The discovery of icosahedral quasicrystal (QC) in rapidly solidified Al-Mn alloy [1] brought about great interest of many researchers. Now there are many atomic structure models of QC, but many of them are far from reality. One of the more simple atomic-structure for Al-Mn-Si icosahedral phase has been offered in [2, 3]. It has been constructed by stacking the Mackay icosahedron (MI). The MI is an atomic cluster of (Al,Si)$_{42}$Mg$_{12}$ with icosahedral symmetry [4, 5]. Recent experimental work [6, 7] showed that the MI with ”glue” atoms successfully reproduced actual atomic configuration of Al-Mn-Si icosahedral phase and that the MI is a basic structural unit of icosahedral and amorphous Al-Mn-Si phases.

Henley and Elser proposed an atomic-structure model for icosahedral (Al,Zn)$_{49}$Mg$_{33}$ paying attention to the similarity of a local atomic structure between the icosahedral phase and Frank-Kasper phase [8]. They showed that atomic structure of (Al,Zn)$_{49}$Mg$_{33}$ in the Frank-Kasper phase could be expressed as a periodic packing of two unit cells (prolate rhombohedra an rhombic dodecahedron) decorated by Al, Zn and Mg atoms.

The more realistic atomic-structure model (quasiperiodic configuration of icosahedral cluster, or QCIC model) of the Al$_6$Mg$_4$Cu icosahedral phase has been proposed in [9]. The structural framework of it is the 3D Penrouse tiling (3DPT) [10]. The basic structural unit in QCIC model is the (Al,Cu)$_{25}$Mg$_{20}$ icosahedral clusters located at twelvefold vertices in 3DPT and the glue atoms which are located between icosahedral clusters. The comparison of the pair-distribution functions $\rho(r)$ of QCIC and Henley-Elser model and x-ray structure factor $S(q)$ with experiment showed the QCIC model is more realistic.
2. Methods and results

The main idea for atomic configuration of QCIC model is that the atomic structure of icosahedral phase was composed of \((Al, Cu)_{25} Mg_{20}\) icosahedral clusters, which are stacked quasiperiodically with "glue" atoms between them. The main difference between QCIC model and Elser-Heley one [11] is that the 3DPT quasilattice is the framework in QCIC model, but it is the bcc lattice in the Elser-Henley model. The 3DPT quasilattice has been obtained by the projection from the six-dimensional cubic lattice to the three-dimensional strip using triacontahedron as a window domain [12]. The algorithm of projection method described in [13] has been used in the Fortran code developed by author (Yu. M). Al and Cu atoms were located on all the vertices and on all the edge centers. The Al and Cu atoms are not distinguished from each other in the present model. Twelvefold vertices with icosahedral symmetry were selected among the vertices of the 3DPT. Twenty Mg atoms were positioned so as to form \((Al, Cu)_{25} Mg_{20}\) icosahedral clusters around twelvefold vertices. Twenty Mg atoms were positioned on the long-body diagonal of every prolate rhombohedron. Two Mg "glue" atoms were positioned at the points dividing the long-body diagonal in the ratio \(\tau : 1 : \tau\) \((\tau = (1 + \sqrt{5})/2)\). The 115 atomic cluster has been taken from obtained atomic structure for calculation both in real and reciprocal spaces.

The self-consistent recursion method in real space [14] has been used for calculation of the electronic structure of \(Al_6 Mg_4 Cu\) quasicrystals. It derives the local density of states (LDOS) from the imaginary part of the diagonal element of Green’s function:

\[
n(E) = -\frac{1}{\pi} \text{Im} G_{00}(E + i\varepsilon_+),
\]

which is given by a continued fraction:

\[
G_{00}(E) = \langle u_0 | (E - \mathbf{H})^{-1} | u_0 \rangle = m(E) - i\pi n(E) = b_0^2/(E - a_0 - b_1^2)/ \ldots b_{n-1}^2/(E - a_n - b_n^2).
\]

The tight-binding linear muffin-tin orbital in the atomic-sphere approximation (TB-LMTO-ASA) formalism has been used for calculation of the Hamiltonian matrix elements [15, 16, 17]. The TB-LMTO Hamiltonian is transformed from the standard LMTO basis to the most localized tight-binding basis. The minimal basis set with s-, p- and d- orbitals have been used in the calculation for all types of atoms. The total density of states (TDOS) has been obtained from the local density of states by means of an averaging procedure. The central part of cluster with 30 atoms has been used for this purpose. The recursion levels were 11, 15, 25 for s-, p-, d-states respectively. The Lucchini-Nex [18] terminator has been used for termination of continued fraction. The Wigner-Seitz radii have been obtained from the electro-neutrality condition by means of serial test calculations. There are two spiky states have been observed at 1.5 and 2 Rydberg below the Fermi level. The convergence in real space is not so good as in reciprocal
space, and therefore about 100 steps were needed in SCF procedure. The obtained TDOS is shown on fig. 1. The total width of the TDOS is equal 10 eV, only one pick we observe in occupied part of it and low DOS on the Fermi level (pseudo gap). It is typical form for almost all quasicrystals.

The \textit{ab initio} Car-Parrinello molecular dynamics (AIMD) \cite{20} in the framework of the density functional theory (DFT) \cite{21, 23, 22} has been used in the reciprocal space calculations. The exchange-correlation term is described by the generalised gradient approximation (GGA) in the Becke-Lee-Yan-Pan (BLYP) implementation \cite{24, 25}. Norm-conserving pseudopotentials \cite{26} with \textit{s} and \textit{p} as nonlocal and \textit{d} as local orbitals were used. The SIESTA code \cite{27, 28, 29} were used in the AIMD calculation. The SIESTA package \cite{s based on flexible linear combination of atomic orbitals (LCAO) basis sets \cite{30}, with actual and efficient Order-N scaling \cite{31}. The cutoff radius was equal 250-Ry, it is guarantee the convergence of the self-consistent procedure to less then 1 meV/atom. The maximum 25 electronic steps were used on the each ionic step in the atomic relaxation procedure. The Parinello-Rahman molecular dynamics \cite{32} with variable shape and volume of the unit cell has been used (NPT ensemble). The same 115 atomic cluster was used as the starting point in SIESTA calculation. The 7 ionic steps were performed during the atomic structure relaxation. The length of supercell was increased on 10\%, the same value were the changes in the atomic coordinates of atoms in the supercell during the atomic structure relaxation. The obtained TDOS with pseudo gap on the Fermi level is shown in the fig. 1. The partial density of states (PDOS) for Al, Cu and Mg atoms are shown in fig. 2 - fig. 4.

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{Al-Cu-Fe_TDOS_in_SIESTA.png}
\caption{TDOS of Al\textsubscript{6}Mg\textsubscript{4}Cu in reciprocal space calculations (SIESTA).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{Al-Cu-Fe_P DOS(Cu) in SIESTA.png}
\caption{Cu PDOS of Al\textsubscript{6}Mg\textsubscript{4}Cu in SIESTA calculations.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{Al-Cu-Fe_PDOS(Al) in SIESTA.png}
\caption{Al PDOS of Al\textsubscript{6}Mg\textsubscript{4}Cu in SIESTA calculations.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{Al-Cu-Fe_PDOS(Mg) in SIESTA.png}
\caption{Mg PDOS of Al\textsubscript{6}Mg\textsubscript{4}Cu in SIESTA calculations.}
\end{figure}
3. Conclusions
The pseudo gap at Fermi level in TDOS is the common feature of all electronic structure of all quasicrystals. The atomic relaxation with 7 ionic steps were needed in SIESTA calculations in order obtain the pseudo gap in TDOS. The analysis of PDOS (fig. 2 - 4) shows the more detail information about electronic structure of QC. The main nearest pick at Fermi level is formed mainly by Cu d- and Al p- states. We may make the conclusion about hybridization of Cu sd- and Al sp- states from the form and positions of it peaks on PDOS. The low conductivity of all quasicrystals may be understood from the fact of the big shift (7 eV) of Al s- states to the occupied part of TDOS. The presence only the p- and d- states at the Fermi level decrease the transport properties of electrons in QC. The spiky states are observed in real space calculations and do not observed in reciprocal space one, they also do not observed in the experiment. There is the extensive discussion in the literature about existence of the spiky states in QC [33]. We believe it is the artificial effect of the recursion method based on LMTO. The main conclusion of this study is as follows. The unique properties of QC are concern to its electronic structure. From the two used methods the \textit{ab initio} MD is more modern and powerful one, but it is very timeconsumer.

Acknowledgments
This work has been supported by RFRF No. 07-03-96122. We are thankful to developer teams the TB-LMTO-ASA and SIESTA 2.0.1 software packages.

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