On the anisotropy in the HRTEM images of a decagonal quasicrystalline phase of the Al-Cu-Co-Si system

R. García-García[a], M.M. Martínez[b], and J. Reyes-Gasga[a,*]
[a]*Instituto de Física, UNAM,*
Apartado Postal 20-364, 01000 México D.F., MÉXICO,
[b]*Instituto Potosino de Investigación Científica y Tecnológica,*
Camino a la Presa San José 2055. Lomas 4ª Secc., 078216 SLP. MEXICO.

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Experimental evidence of an electrical and/or magnetic anisotropy was observed in the high resolution transmission electron microscope (HRTEM) images of a decagonal quasicrystalline (DQC) phase of the Al-Cu-Co-Si system. X-ray energy dispersive spectroscopy (EDS) spectra indicated a composition of $Al_{60}Cu_{23}Co_{15}Si_2$ for this phase. The anisotropy was responsible for poor contrast quality in the HRTEM images along the periodic direction of this phase, whereas good image contrast was observed in the quasi-aperiodic ten-fold plane. Comparing these results to findings previously reported for the $Al_{62}Cu_{20}Co_{15}Si_3$DQC, we conclude that the observed anisotropy is strongly dependent on the selected chemical composition. After analyzing both the electrical and magnetic effects presented by a sample which is observed with an electron microscope, we conclude that the electrical properties of the DQC phase might be responsible for these observations.

Keywords: Electron microscopy; decagonal quasicrystalline phase; EDS analysis; quasicrystals.

Evidencia experimental de una anisotropía eléctrica y/o magnética ha sido observada en imágenes de microscopio electrónico de transmisión de alta resolución (HRTEM) del sistema decagonal Al-Cu-Co-Si de fase quasicristalina (DQC). Espectroscopía de energía rayos-X dispersados(EDS) indica que la composición de esta fase es $Al_{60}Cu_{23}Co_{15}Si_2$. La anisotropía es responsable de la pobre calidad de contraste en las imágenes HRTEM a lo largo de las direcciones periódicas de esta fase, mientras que el buen contraste de imágenes fue observada en los planos quasi-periódicos decagonales. Comparando los presentes resultados y los anteriormente reportados para la fase DQC $Al_{62}Cu_{20}Co_{15}Si_3$. Concluimos que la anisotropía observada, es fuertemente dependiente de la composición química específica . Después de analizar los efectos magnéticos y eléctricas presentados por una muestra al observarse en el microscopio electrónico, concluimos que las propiedades eléctricas de la fase DQC podría ser la responsable de estas observaciones.

Descriptores: Microscopía electrónica; fase cuasicristalina decafonal; análisis EDS; cuasicristales.

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1. Introduction

Physical properties of quasicrystals (QC) have opened up an interesting field of study in materials science [1,2]. In particular those QC phases that have shown anisotropies in properties such as electronic transport, electrical conductivity, Hall effect, thermo-electrical power, and thermal conductivity, which are not well understood yet [2,3]. For example, the stable icosahedra QC phase in Al-Pd-Re, Al-Pd-Mn, Al-Cu-Ru, and Al-Cu-Fe alloys has been reported with a temperature dependent electrical conductivity which increases when temperature increases. In the Al-Cu-Co-(Si) system the QC phases were reported with strong variations in electrical conductivity with a very slight change in composition [3].

Transport anisotropy in the Al_{62} Cu_{20} Co_{15} Si_3 decagonal QC (DQC) phase was reported by Lin Shu-yuan *et al.* [4]. They reported a linear dependence of the resistivity with temperatures from 80 to 400 K for both periodic and quasi-periodic directions but with negative thermal conductivity coefficients. However Shibuya *et al.* [5] measured a positive thermal conductivity in the Al_{70} Ni_{15} Co_{15} DQC phase in both directions from 4 to 300 K. The specific heat and thermal conductivities of the $Al_{65}Cu_{15}Co_{20}$DQC phase were measured at low temperatures (0.45K -105 K) by K. Edagawa *et al.* [6] along the periodic and quasi-periodic directions. In this case they indicated that the phonon contribution to the total thermal conductivity along the periodic direction showed behavior similar to that of periodic crystals, but there were some variations along the quasi-periodic direction. Thermoelectric power was also reported as positive in the periodic direction and negative in the quasi-periodic plane of this DQC phase [6].

The resistivity in the Al_{65} Cu_{15} Co_{20} and Al_{70} Ni_{15} Co_{15} DQC phases was measured from 4 to 600 K by Shu-yuan et al. [4] and Martin *et al.* [7], and they observed a metallic behavior along the periodic direction and nonmetallic along the quasi-periodic direction. Many authors agree that the conductivity in the QC plane of the DQC phase is very low ($\sigma_p/\sigma_q \approx 50 - 150$ at low temperatures) but it increases with temperature and composition [3]. Hall conductivity has also been reported that is anomalous. Yun-ping *et al.* [8] measured it in the DQC phases of the Al-Ni-Co, Al-Cu-Co and Al-Si-Cu-Co systems, finding a slight dependence with temperatures between 80 and 330 K. Moreover, the Hall coefficient R_H changed sign when the magnetic field was rotated 90° from the tenfold axis. In fact, they indicated that the anisotropy observed by Zhang Dian-Lin *et al.* [9] in Al-Si-Cu-Co is a universal property for materials with decagonal QC symmetry because of the strong interaction of the Fermi surface with the quasi- Brillouin Zone boundaries.

Most of the QC alloys exhibit diamagnetic, paramagnetic and spin-glass properties. Ferromagnetic and magnetic properties have been reported to be anisotropic for some QC systems [10]. Satoh *et al.* [11], for example, measured the magnetic moment of the icosahedral and decagonal phases in Al_{70} Pd_{30-x} Mn_x and found that the saturation moment for icosahedral phase is higher than for the decagonal phase. Markert *et al.* [12] carried out a dc magnetization and electrical resistivity analysis of a single-domain of Al_{70} Ni_{15} Co_{15} DQC phase and reported a weak anisotropy for their magnetic properties. Added to this, a small ferromagnetic component, a Curie-like component, and a weak super-conducting transition at T=3.2 K were observed. Anisotropic magnetic properties for the Al_{72} Ni_{12} Co_{16} DQC phase were also reported by Yamada *et al.* [13]. They found that this quasicrystal is essentially diamagnetic with an anisotropic susceptibility of 2.0 $\times$ 10^{-7} emu/(g.Oe) along the quasi-periodic plane and -3.7 $\times$ 10^{-7} emu/(g.Oe) along the periodic axis.

The magnetic susceptibility and diamagnetic behavior for crystalline phases Al_{70} Ni_{15} Co_{15} and Al_{62} Cu_{20} Co_{15} Si_3 have been also reported elsewhere [14]. However, according to the data given in Ref. 14, at room temperature (RT) the resistivity is still rather low, 63 microOhm/cm along the periodic direction and 510 microOhm/cm in the quasi-periodic plane. At RT, this did not change drastically with the composition and is of the same order of approximation. The susceptibility of Al-Cu-TM (TM, transition metals) and Al-Pd-TM quasicrystalline alloys was measured in the temperature range from 4.5 to 270 K. A temperature-independent contribution of χ_o and a Curie-Weiss contribution $(\chi - \chi_o)$ =C/(T – θ) was obtained in all cases, but with a negative value of θ, which implies anti-ferromagnetic interactions. In Al_{65} Cu_{15} Co_{20}, Al_{70} Pd_{10} Co_{20} and Al_{72} Pd_{20} Cr_8 alloys, a remarkable dependence on temperature was found [15]. Lück and Kek [16] carried out measurements of temperature dependence of the magnetic susceptibility on decagonal phases Al_{65} Cu_{15} Co_{20} and Al_{70} Ni_{15} Co_{15}. They obtained a diamagnetic behavior at room temperature, which changes to paramagnetic when the temperature increases.

HRTEM images are very sensitive to the electrical and/or magnetic conductivity properties of the sample. In this work we report an anisotropic behavior for the periodic and quasi-periodic directions of the DQC phase of the $Al_{62}Cu_{20}Co_{15}Si_3$ alloy. It is shown that this anisotropy was responsible for the shift observed in the electron microscope when the sample was oriented along either of the two periodic directions of this QC phase, resulting in poor contrast HRTEM images. These results are complementary to those reported in the previous work by Lara *et al.* [17], where the $Al_{62}Cu_{20}Co_{15}Si_3$DQC phase was successfully analyzed with good images of the periodic directions obtained by HRTEM.

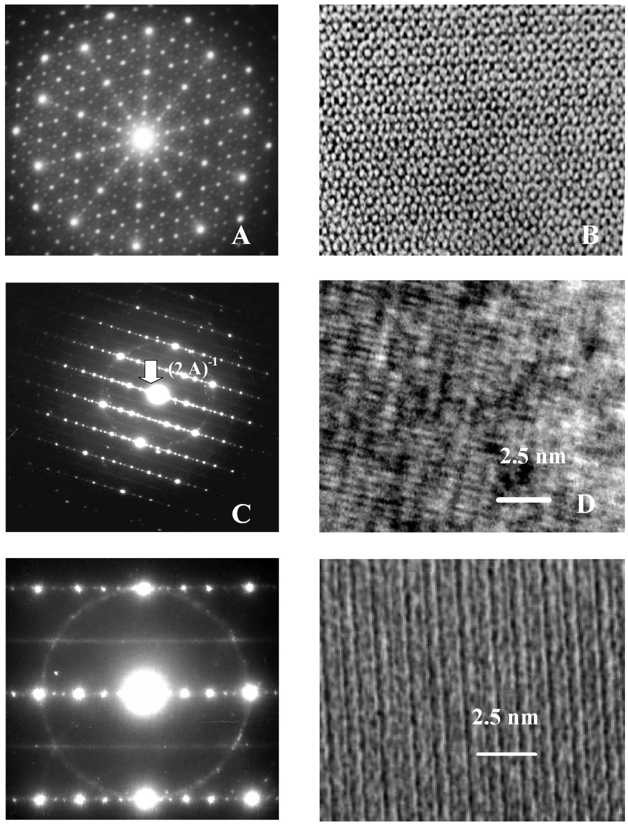

FIGURE 1. A) Selected area diffraction pattern of the decagonal quasicrystalline phase and their corresponding HRTEM images. A-B) Ten-fold direction. C-D) D-two-fold direction. E-F) P-two-fold direction. In the case of the two-fold directions, the HRTEM images are the best ones recorded because the instability that they always presented.

2. Experimental procedure

Melting the constituent elements in amounts corresponding to their atomic ratio, an $Al_{62}Cu_{20}Co_{15}Si_3$ alloy was made. The melting and growth processes were carried out in a double elliptical mirror furnace as reported elsewhere [17, 18]. The radiation of a 600 W halogen lamp was focused on the sample by elliptical mirrors heating it at 1600 K for 120s on the top of a rotational graphite substrate (in an argon atmosphere) and cooled to room temperature in approximately 300s. During heating the sample took the shape of a spherical drop and convection currents mixed the components. A one-centimeter-diameter solid spherical drop was obtained and broken into two pieces by bare-hands. The SEM, X-ray and X-ray EDS analysis of this spherical drop has already been reported [19].

One of the parts was ground and the powder was supported in holey carbon copper grids for TEM analysis. An analytical electron microscope JEOL TEM 100CX operated at 100 KV was used for conventional TEM observation. Electron diffraction patterns were obtained using a $\pm$ 60° goniometer and a double tilt holder. For HRTEM observation, a JEOL HRTEM 4000EX microscope with a 0.17 nm point-to-point resolution and operated at 400 KV was used. This microscope has a "cold finger" device which permits the observation of the sample at liquid nitrogen temperature (73 K) and reduces the contamination process of the sample. Characteristic x-ray EDS analysis was obtained with a JEOL TEM 2010 microscope that has NORAN EDS equipment attached.

3. Results

The presence of the decagonal QC phase was confirmed by selected area diffraction patterns (Fig. 1). This phase was characterized by the periodic parameter c*=0.4nm. In grains with a decagonal structure, the composition measured with EDS was $Al_{60}Cu_{23}Co_{15}Si_2$ [19]. Their HRTEM images along the ten-fold axis show the well-known contrast features (Figs. 1a and b). However, along the ten-fold axis any image shifts have a good quality presentation. On the other hand, when a HRTEM image was to be taken from any of the two 2-fold axes, some image distortion appeared because the sample was never stable. This happened even at the temperature of liquid nitrogen (73 K). The best images along these directions (Figs. 1c-e) were taken with the help of the computer image program SYS, which is on-line with the microscope JEOL-4000EX. The quality of these images can be compared with those shown in Figs. 7 and 8 of the decagonal phase along the two 2-fold axes in Ref. 18. The truth is that there is no point of comparison.

The electron microscopy analysis reported in Ref. 18 never showed any shift such as the one observed in this work. This indicates the existence of a type of electrical and/or magnetic behavior in the two 2-fold axis periodic planes that does not exist in the ten-fold axis plane. Comparing the EDS results of those reported in Ref. 18 ($Al_{62}Cu_{20}Co_{15}Si_3$) with those reported in Ref. 19 ($Al_{60}Cu_{23}Co_{15}Si_2$) for the sample reported in this work, it is clear that this behavior depends on the chemical composition of the DQC phase.

4. Discussion

The fact is that there are differences in the electrical and/or magnetic behavior between the two two-fold and the ten-fold axes of the DQC phase which are a function of its chemical composition. These differences affect the kind of interaction between the electron beam and the sample that will result in a poor quality of the HRTEM images. We visualize this behavior from both the electrical and magnetic points of view in the following way.

i) Magnetic effect

If the sample produces a magnetic field of such intensity that it could modify the trajectory of the electron beam, this modification will result in resolution loss in the microscope. Let $\mathbf{B}_k$ be the component of the total magnetic field produced by the QC sample, e the electron charge, and $\mathbf{V}_j$ its velocity in the beam, and ε_{ijk} the Levi-Civita tensor; then the Lorentz force is given as:

$$\mathbf{F}_i = e\varepsilon_{ijk}\mathbf{V}_j\mathbf{B}_k$$

The main effect of $\mathbf{F}_i$ on the beam trajectory is to change its direction, producing a perturbation shown in the shift observed in the HRTEM images. The magnetic field produced by the QC sample should be strong enough in the conditions of the TEM operation (73 K when the cold finger device was used and a vacuum of 10^{-10} Torrs). If the magnetization vector were parallel to the 10-fold symmetry so that the sample was observed along the periodic direction, the environment would have a maximum of magnetic force deviation in the electron beam.

ii) Electrical effect

In the case of the electrical anisotropy, the electron beam is modified in the trajectory due to the electrical charge of the sample. This is a common situation in dielectric samples such as ceramics, where a very low density of charge is enough to produce this kind of behavior in the sample-electron beam interactions. So the electron beam might suffer a charge effect in the DQC phase under the observation conditions of the microscope (73 K when the cold finger device was used and a vacuum of 10^{-10} Torrs).

If the magnetic field is not strong and Hall contributions are negligible the electrical current in the sample would not have thermoelectric contributions and the fallowing considerations are valid.

If the electric field is $\mathbf{E}_i$ produced by the total accumulated charge in the DQC phase of a conductivity g_{ij} , the current density $\mathbf{J}_j$ in the material is given by,

$$\mathbf{J}_j = g_{ji}\mathbf{E}_i$$

where g_{ij} is a second rank tensor and, in the case of the DQC phase, its symmetry is related to the point group of the decagonal phase. If we choose the Z-axis of the coordinate system along the periodic axis of the decagonal QC phase so that the XY-plane is in the ten-fold QC plane, the nine components of the electric conductivity tensor are:

$$g_{ij} = \begin{pmatrix} g_{xx} & g_{xy} & g_{xz} \\ g_{yx} & g_{yy} & g_{yz} \\ g_{zx} & g_{zy} & g_{zz} \end{pmatrix}$$

From here we have 3 possibilities:

I. When the electrical field is parallel to the Z–axis, the expression for **J** gives:

$$J_x = g_{xz}E \quad J_y = g_{yz}E \quad J_z = g_{zz}E$$

The combination of J_x and J_y gives the effective current in the QC plane and J_z goes along the electrical field.

II. When the electric field is in any specific direction and the material structure is such that the tensor-matrix is a diagonal matrix produced by high symmetry of the sample, then we have:

$$J_x = g_{xx}Ex, \quad J_y = g_{yy}E_y \quad J_z = g_{zz}E_z$$

Again, the combination of J_x and J_y gives the effective current perpendicular to the crystalline planes which are parallel to the Z-axis, and J_z follows the periodic axis.

III. When the electric field is along Z-axis and g_{ij} is a diagonal matrix, then Jz is present and any anisotropy effect is generated.

It is clear that any of these contributions I, II, III will modify the beam going through the sample of DQC producing some of the anisotropies observed.

5. Final Remark

The experimental observations presented here indicate that the images taken along the periodic directions of a DQC can be improved upon. The anisotropy of the conductivity tensor, g_{ij}, will be affected to different degrees, depending on the crystallographic orientation of each phase, as specified by cases I and II. The observed anisotropy is a strong function of the chemical composition, and the crystallographic symmetry of the alloy. We can conclude that the anisotropy of the HRTEM images has an electrical origin, and the observed shift is a result of the magnetic effects.

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∗. Contact Author: Tel. (525) 622-5048, Fax. (525) 622-5050, e-mail: ramiro@fisica.unam.mx

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