Effect of swift heavy ion irradiation on quasicrystalline materials

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Abstract

The effect of swift heavy ion irradiation (SHII) on quasicrystalline Al5Cu33Fe15 is reported for the first time. This particular quasicrystal is chosen for this study, so that the effect of electronic excitations on the intrinsic electronic properties of quasicrystals can be studied. It is found that irradiation at 77 K improves the quasicrystalline order and results in icosahedral grain growth. These results provide experimental support to the view that the quasicrystal structures can be described as hierarchy of overlapping connecting clusters.

1. Introduction

Swift heavy ions passing through a solid lose energy mainly through inelastic collisions of ions with the electrons in the material. The electronic stopping power corresponding to the inelastic collisions is the dominant factor governing energy loss. For this very reason, SHII seems to be an attractive tool to excite the electronic structure of quasicrystals and investigate the corresponding effect on them. Quasicrystals are metallic compositions that have no periodicity but have long range order. Electronic structure of quasicrystals is still not very well understood. Various models exist in literature which attempt to give possible description of electrons in quasicrystals.

It has long been recognized [1] that defect production/defect annihilation (DP/DA) by swift heavy ion irradiation (SHII) in many metals (like Ni, Ni3B, Ni3Fe and some amorphous materials) is possible only above an electronic stopping power threshold \( \sim 1.5 \) keV/Å, although the details of the mechanism of defect creation by SHII is not well understood. The present level of understanding in this direction is well summarized by Dunlop et al. [2] with the suggestion that the density of states (DOS) at the Fermi energy, \( E_f \), probably determines whether the material would be affected by the electronic excitations produced by SHII. A high density of states (DOS) at \( E_f \) is expected to favor an efficient coupling between excited electrons and lattice atoms and thus favorably induce DP/DA.

In order to determine the importance of the DOS at \( E_f \) as a criterion for DP/DA by SHII in metallic materials and also to fill the gap
between the studies on amorphous and crystalline materials, we have investigated the stable quasicrystal Al$_{46}$Cu$_{30}$Fe$_{15}$. Although low energy (~1 MeV) electron irradiation studies leading to damage formation by elastic collisions of ions with the frozen atomic sites have been reported for quasicrystals by Urban and co-workers [3,4], the current study is the first attempt to understand the effects of SHII on these materials. Unlike the situation for low energy irradiation, the inelastic collision of ions with electrons in target material which occur during SHII are expected to provide electronic excitations leading to structural changes. Quasicrystalline Al–Cu–Fe alloys are of particular interest as it is known [5] that the electrical resistivity is a sensitive function of the degree of atomic disorder and that increasing disorder leads to decreasing resistivity, in contrast to the typical situation in crystalline materials. The composition used in the current work was chosen for the following reasons:

(a) it remains stable up to a very high temperature (1135 K) [6] and
(b) it has a very small density of states (DOS ~0.14 states/eV atom) [5] near $E_F$, much smaller than the DOS for Cu and Ni samples studied by Dunlop et al. [2].

For the above reasons it is anticipated that this material will help to elucidate the effects of SHII on quasicrystalline materials and to provide additional information about the mechanism of DA/DP by SHII, particularly with respect to the influence of the DOS at the Fermi energy.

2. Experimental methods

The quasicrystalline Al$_{46}$Cu$_{30}$Fe$_{15}$ alloy was prepared by arc melting high purity elemental constituents in the desired stoichiometric proportion [7]. For the present work, the as-cast sample was used. The quasicrystal structure was verified by X-ray (XRD) measurements using CuK$_\alpha$ radiation (Fig. 1(a)). For the irradiation experiment, the sample was held at 77 K and irradiation was interrupted in order to make in situ resistivity versus fluence measurements. From TRIM [8] calculations, it is expected that 100 MeV Ni ion beam would have electronic energy loss of ~1.3 keV/Å near the surface and the ion penetrate up a depth of about 10 μm in this material. Adequate care was taken to measure the resistivity in the region of the sample that was subject to irradiation. At 77 K the atomic mobility in quasicrystals is negligible and this facilitates DP/DA. The thickness of the sample (20 μm) was larger than the projected range of the ions (≈10 μm), hence the ions are expected to stop within the specimen. However, the number of Ni ions thus introduced in the target on irradiation is less than 2 ppm. This point is discussed further below.

![Fig. 1. X-Ray Diffraction patterns of (a) as cast Al$_{46}$Cu$_{30}$Fe$_{15}$; (b and c) both sides of irradiated Al$_{46}$Cu$_{30}$Fe$_{15}$.](image-url)
3. Results and discussion

The measured resistivity, $\rho$, of quasicrystalline $\text{Al}_{1.5}\text{Cu}_{0.5}\text{Fe}_{1.5}$, before and after irradiation are shown in Fig. 2 for the temperature range $77 \text{ K} < T < 300 \text{ K}$. The inset of this figure (Fig. 2) shows the resistivity down to $4 \text{ K}$ measured on the irradiated sample. The inset of Fig. 3 shows the $\rho$ versus $\phi$ (fluence) curve. These data show that irradiation with a fluence greater than about $4 \times 10^{13}$ ions/cm$^2$ produces an overall increase in resistivity by more than a factor of 2 at $77 \text{ K}$. It is interesting to note that the changes introduced in the sample by SHII do not appear to be reversible at room temperature, as a sample held at this temperature for a period of about 3 weeks after irradiation showed results which were identical to those of the freshly irradiated sample. The low temperature resistivity of the irradiated sample (see inset of Fig. 2) shows a peak in the resistivity at about $20 \text{ K}$ and corresponds to a value of $\rho \approx 4515 \mu\Omega \text{ cm}$ which is comparable to the highest quoted values in the literature [9], corresponding to the samples with the highest degree of structural and chemical order. The relationship of resistivity on fluence as measured at $77 \text{ K}$ (see Fig. 3) shows that the resistivity initially increases with fluence but after a critical value (about $2.5 \times 10^{13}$ particles/cm$^2$) becomes almost constant.

![Fig. 2. Resistivity of $\text{Al}_{1.5}\text{Cu}_{0.5}\text{Fe}_{1.5}$ measured as a function of temperature before (solid circles) and after (open circles) irradiation. Inset shows resistivity versus temperature for irradiated sample, down to $4 \text{ K}$.

Fig. 3. Differential defect annihilation curve, $d(\Delta\rho)/d\phi$ versus $\Delta\rho$ (DDAC). Inset shows resistivity as a function of fluence at $77 \text{ K}$.

The general features of the $\rho$ versus $T$ data as obtained in the present work both before and after irradiation include high values of the resistivity, a negative temperature coefficient of resistivity and a positive curvature. These features are consistent with results reported previously for high quality quasicrystalline samples and are well explained by quantum interference effects [10]. However, it is important to note that due to large resistivity values in the sample, particularly at low temperatures, even very small inclusions of a comparatively better conductor (such as the Ni stopped within the sample) can short circuit the intrinsic electron transport. Thus, the values of $\rho$ reported here for the irradiated sample must be considered as minimum values for the actual quasicrystalline phase present. The relatively low values of the resistivity of the un-irradiated sample indicates a substantial quantity of intrinsic defects present [5]. The overall two-fold increase in resistivity on irradiation which is observed over a wide range of temperatures is indicative of a drastic reduction in defect concentration, comparable to that obtained during the usual high temperature annealing procedure typically applied to these materials [6,7]. This behavior may be understood in terms of defect recovery that results from electronic excitations produced by SHII.

The XRD measurements of the irradiated sample were done to verify icosahedral structure.
The results (Fig. 1(b) and (c)) show that the effect of SHII with fluence of $2 \times 10^{13}$ particles/cm$^2$ is equivalent to the annealing of the quasicrystals [6,7] at very high temperatures over an extended period of time. The glancing angle XRD (GAXRD) at 3° and 5° on irradiated sample (Fig. 4) was also done to verify that the annealing effect is distinctly visible within a few μm range near the surface, where the effect of electronic energy loss is maximum. During the passage of swift heavy ion moving with Bohr velocity of electrons of the materials, the electrons are strongly attracted by the highly charged SHI along the direction of the movement and it is generally noticed that these electrons move much farther than the ion range along the ion trajectories [11]. This is reflected in our results showing the variation of resistivity as a function of temperature before and after irradiation (Fig. 2) and as a function of fluence at 77 K (inset of Fig. 3).

Comparing the XRD patterns of as-prepared and irradiated samples and especially the GAXRD data that looks for the structural changes only on the top few μm thickness of the sample where electronic excitation effect is predominant, one can say with conviction that as a result of SHII, the electronic excitations in quasicrystals has induced ordering in the structure.

The details of defect annihilation (DA) induced by SHII in quasicrystals may be explained by a simple model [2]. It is assumed that the Ni ions, of flux $\Phi$, transfer their energy to the quasicrystal within a cylinder of cross-sectional area $S_1 = \pi r_1^2$, causing electronic excitations which create a small concentrations of quasi-interstitials around this trajectory. These interstitials are free to migrate in the quasi lattice within the recombination volume between two coaxial cylinders of radii $r_1$ and $r_2$ and recombine readily with the quasi vacancies (which are expected to be formed). If $F_1$ is the fraction of defects in the defect cylinder with radius $r_1$ and $F_2 = 1 - F_1$ is the fraction of annihilated defects with the reduced defect cylinder radius $r_2$, then we can write,

$$dF_1 = (1 - F_1)S_1d\Phi - S_2F_1d\Phi.$$ 

If $C$'s denote the concentration of defects and we say

$$C = C_1 F_1 \quad \text{then} \quad \dot{C} = C_1 \frac{dF_1}{d\Phi} \quad = S_1 C_1 - (S_1 + S_2)C.$$ 

The difference in resistivity before and after irradiation, $\Delta \rho$, is also expected to be proportional to the resistivity caused by DA. Fig. 3 shows the differential defect annihilation curve (DDAC), $\Delta \rho = d(\Delta \rho)/d\Phi$ versus $\Delta \rho$. The values of $\Delta \rho$ were obtained from $\rho$ versus $\phi$ graph in the inset of Fig. 3, then from a $\Delta \rho$ versus $\phi$ plot (not shown here) $\Delta \rho = d(\Delta \rho)/d\Phi$ values were calculated and DDAC was plotted. The important parameters are initial defect annihilation rate, $\Delta \rho_0 = d(\Delta \rho)/d\Phi|_{\phi=0}$ and the saturation resistivity increase, $\Delta \rho_{sat} = \Delta \rho|_{\phi=0}$, directly related to $C_0 = S_1C_1$ and $C_{sat} = [S_1C_1/(S_1 + S_2)]$. The values of $r_1$ and $r_2$ calculated from DDAC are given by

$$r_{1\text{min}} = [\Delta \rho_0/(\pi \Delta \rho_{sat})]^{1/2}$$

and

$$r_2 = [\Delta \rho_0/(\pi \Delta \rho_{sat})]^{1/2},$$

where $\Delta \rho_{sat}$ represents the value of $\Delta \rho$ due to low energy irradiation. In the absence of an experimental value of $\Delta \rho_{sat}$ we have used the minimum resistivity value at 77 K before irradiation. This yields values of $r_1 = 11.1$ and $r_2 = 8.8$ Å. Clearly the defects around the trajectory of Ni have thus been annealed and the defect cylinder has shrunk.

Fig. 4. Glancing angle X-ray Diffraction (GAXRD) on irradiated Al$_6$Cu$_5$Fe$_{13}$. 
In quasicrystals such electronic excitation induced defect annihilation is thus expected to be quite strong (τ₁;τ₂ is large) and accordingly we could verify the DA process on both sides (irradiated surface and the other side) by X-ray diffraction.

The observation that AlCuFe, despite having a very low density of states and a weak electron-phonon interaction, still shows the effects of DA and SHII results in a highly ordered quasicrystalline phase with increased resistivity; gives support to the view that quasicrystals respond via a local mechanism. The structure of quasicrystals can be thought of as an icosahedrally ordered aggregate of connecting atomic clusters [12] where electrons are confined to a deep potential well induced by the positive ions of the clusters. The electronic excitations caused by SHII induces the hopping of electrons from within a cluster to an inflated square well. This process continues with increasing fluence, connecting more and more clusters. At each stage the electrons are confined to a larger well by a barrier that is more difficult to cross. In this way the average number of electrons per atom decreases with increasing fluence until a critical fluence is reached and the process is stabilized. Thus irradiation results in an increase in order which for quasicrystalline materials is observed as an increase in the resistivity at all temperatures.

4. Conclusions

In conclusion, it has been shown that the quasicrystal structure, being an aggregate of overlapping clusters, is highly susceptible to the electronic excitations as explained above. Thus SHII provides unique conditions for defect annihilation processes in quasicrystalline materials and the present results show a resulting increase in resistivity characteristic of the elimination of defects.

We must point out here that our results are still at a preliminary stage. There are several factors that still need improvement. One of the major point that needs to be tailored is the thickness of the target material in comparison to the calculated electronic excitation range. Target being thicker than the electronic excitation range, Ni ions are expected to stop within the material. This would then introduce nuclear collision related defects that would generate at the end of the excitation range. So, although it can be said with certainty that the annealing effect shown by GAXRD is solely due to the electronic excitations in the material, this is not true for the resistivity measurements. Resistivity being the bulk property of the material, gives us an average effective value contributed by both electronic and nuclear collisions. Experiments on thinner foils of more perfect quasicrystalline materials, e.g., Al₂₅Cu₂₅Fe₁₂₅ and AlCuRu, which show a range of density of state values are currently in progress to better understand the relationship of DA and electronic excitations in these materials.

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References