行政院國家科學委員會專題研究計畫 成果報告

(AgIn)_{100-x-y}MgxRE_y 準晶的合成及稀土元素對準晶電、
磁、熱性的影響
研究成果報告(精簡版)

計畫類別：個別型
計畫編號：NSC 94-2112-M-006-019-
執行期間：94年08月01日至95年10月31日
執行單位：國立成功大學物理學系（所）

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處理方式：本計畫可公開查詢

中華民國 96年01月26日
Studies of the formation, electrical resistivity, and surface oxidation of Ag-In-Mg-Yb quasicrystals

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Abstract

The electrical resistivity of the studied Ag-In-Mg-Yb quasicrystals all increases with the decrease of temperature. i.e., their resistivity ratios $R = \frac{\rho(4.2K)}{\rho(300K)}$ are all greater than one. The low-temperature resistivity of Ag-In-Mg-Yb QCs was found to reduce as the samples were aged in air at room temperature. In this work, we clearly show that this is attributed to the oxidation of sample surface. Using a SEM in a BSE mode to examine the sample surface, we found that the oxidation mainly results from Yb elements and In and/or Ag elements are possibly pushed to the edge of the oxidized areas as the Yb oxide was formed. Thus, we think the formation of Yb oxide starting on the sample surface could at the end destroy the quasicrystalline structure and cause the precipitation of Ag and/or In-containing metallic phase and therefore, lead to the reduction of the low-T resistivity. We also found that the Ag-In-Mg-Yb samples prepared by an induction furnace have the true composition close to the nominal composition than those prepared by an arc furnace. This makes it easier to study the composition dependence of the physical properties of quasicrystals.
摘要

Ag-In-Mg-Yb 準晶的電導率均隨溫度降低而升高，也就是它們的電阻比 $R = \frac{\rho(4.2\text{K})}{\rho(300\text{K})}$ 均大於 1，這是高品質的金屬態準晶常見現象，這種現象可用量子干涉效應來解釋。Ag-In-Yb 準晶在低真空曝露太久(即老化(aging)的意思)，其低溫電阻會下降。我們發現這是樣品氧化的緣故。

利用掃描式電子顯微鏡觀察被氧化的表面，發覺氧化來自於 Yb 元素，而且 Yb 的氧化物會將 In、Ag 推擠到被氧化區域的邊緣。因此我們認為 Yb 的氧化會破壞準晶的結構，和引起含有 Ag 和 In 組成的金屬相或單獨的 Ag 及 In 金屬析出，是導致低溫電阻的下降的原因。

我們發現利用感應爐所製成的 Ag-In-Mg-Yb 準晶樣品，其實際成分都比用電弧爐製成的樣品更接近配方的成分(nominal composition)，因此用前一方法所製成的樣品較方便用來研究準晶物性與成份的變化關係。
I. Introduction

In 2002 Guo et al. first used equal proportion of Ag and In to replace Cd in Cd$_{84}$Yb$_{16}$ to form (AgIn)$_{84}$Yb$_{16}$ quasicrystals (QCs); subsequently, we studied the electrical, magnetotransport and thermal properties of Ag-In-Yb QCs and found that good quality Ag-In-Yb QCs should satisfy the following conditions: (a) The resistivity ratio $r = \rho (4.2 \text{ K})/(300 \text{ K})$ must be larger than 1; (b) the magnetoresistance $\Delta \rho (4.2 \text{ K}, H)/\rho (4.2 \text{ K})$ should be less than 0.1%; the volumetric proportion of superconductors (In) is close to zero. Additionally, we found that their low-T resistivity drops seriously as the sample aged in in the air at room temperature.

In this work we will study the effects of Mg on the electrical properties of Ag-In-Yb QCs and employ the SEM to investigate the effects of the surface oxidation on the electrical properties of Ag-In-Yb QCs.

II. Experimental procedures

Ingots of (AgIn)$_{42.25-x}$Mg$_x$Yb$_{15.5}$ and (AgIn)$_{100-x}$Yb$_x$ ($15 < x < 16$) were prepared by arc-melting a mixture of high purity constituent elements, Ag (99.99%), In(99.99), Mg(99.99%), and Yb(99.99%) in purified argon atmosphere, and then the ingots were subsequently annealed at 400-450 $^\circ$C for 50-100 h. For comparison, these Ag-In-Mg-Yb QCs were also prepared in an induction furnace. X-ray diffraction spectra were recorded using a rotating-anode $x$-ray generator (Cu k $\alpha$, 50 kV, 120 mA) with a graphite (002) monochromator. The resistance measurements were performed from $4.2$ K to $300$ K using a Linear Research LR 700-AC resistance bridge (15.9 Hz). And magnetic susceptibility was measured by SQUID.

III. Results and discussion

(A) Resistance

(a) For Ag-In-Yb QCs

X-ray spectra show all the measured samples are single-phased QCs. The averaged value of the quasilattice constant for Ag-In-Yb QCs is about 5.5932 A, and averaged value of the resistivity at $4.2$ K is around 2.534 m$\Omega$·mm.

Fig. 1 shows the normalized resistivity $\rho (T)/\rho (300 \text{ K})$ as a function of temperature for (AgIn)$_{42.5}$Yb$_{15}$, (AgIn)$_{42}$Yb$_{16}$, and (AgIn)$_{42.25}$Yb$_{15.5}$ QCs. The resistance for all the
studied samples is seen to increase as the temperature is reduced, exhibiting the weak localization behavior widely observed in metallic QCs. The resistance $\rho(T)$ vs temperature for $Ag_{42.61}In_{42.46}Yb_{14.9}$ (Fu 51), $Ag_{41.95}In_{42.57}Yb_{15.48}$ (Fu 87), and $Ag_{42.02}In_{41.99}Yb_{15.99}$ QCs is displayed in Fig. 2; the results indicate that the resistivity decreases with increasing Yb concentration.

(b) For $(AgIn)_{42.25-x}MgxYb_{15.5}$ QCs

$(AgIn)_{42.25-x}MgxYb_{15.5}$ QCs with nominal compositions are prepared in both a arc furnace and an induction furnace. The actual compositions of the samples prepared by the latter method is much closer to the nominal compositions than those samples prepared by the former method. Fig. 3 shows the $\rho(T)/\rho(300 K)$ plotted against $T$ for $(AgIn)_{42.25-x}MgxYb_{15.5}$ QCs prepared in a arc furnace and an induction furnace respectively. It is seen that except for the sample (Al 129) with $x = 10.5$ prepared by the induction method, all the measured resistivity increases with decreasing temperature as observed in Ag-In-Yb QCs. The drop in the resistivity below 50 K in Al 129 sample, we found, is possibly due to the precipitation of $(AgMg)$ impurity as revealed at the diffraction angle $2\theta = 38.25^\circ$, as shown in the x-ray spectra (Fig. 4). The quasilattice constant vs Mg content for $(AgIn)_{42.25-x}MgxYb_{15.5}$ QCs prepared by different methods is shown in Fig. 5. The quasilattice constant is seen to increase monotonically with increasing Mg concentration in the samples prepared by the induction method, however, the quasilattice constant does not change orderly with the increase of Mg content in the samples prepared in a arc furnace. This, we think, is due to the fact that the actual compositions is quite different from the nominal compositions in the samples prepared in a arc furnace.

(B) Effects of aging on the electrical properties of Ag-In-Yb QCs

The reduction in the low-T resistivity in the samples aged in the air was found by us. To understand the causes and the mechanisms which lead to the decrease of the low-T $\rho$, we cut a fresh $Ag_{42.5}In_{42.5}Yb_{15}$ sample into two parts; one is called Fu53a and the other is Fu53-1. The fresh sample is defined as the sample prepared within 5 days. The resistivity of both fresh sample was measured and the results are shown in Fig. 6. The surface of the Fu53a sample was then coated with gold to prevent oxidation. Both Fu53-1 and Fu53a (one coated with gold) were aged in low vacuum ($10^{-2}$ torr) for 150 days, then their resistivities were measured again, also shown in Fig. 6. The unchanged in the the resistivity in the Fu53a sample before and after aged is obviously seen; while for the aged Fu53-1 sample, its resistivity drops clearly at low T. This implies that the reduction in low-T resistivity in the aged Fu 53-1 is closely related to the surface oxidation of the sample.

(C) Investigation of the surface of the aged sample
Figs. 7 and 8 show the EDS mappings of O, Ag, In, and Yb elements in the fresh Fu53-1 and Fu53a samples. From the distribution of these elements, we can say both samples are homogeneous. The SEM images of the aged Fu53a (gold layer removed), aged Fu53-1 samples and fresh Fu53-1 sample are shown in Fig. 9. The surface is observed to be smooth in both aged Fu53a and fresh Fu53-1 samples, but cracks are easily seen on the surface of the ages Fu53-1 samples. This suggests that gold layer does protect the surface of the Age Fu53a from oxidation; and implies the reduction in low-T resistivity in the aged samples is closely related to the surface oxidation. The SEM images at different magnifications of the ages Fu53-1 sample are exhibited in Fig. 10. The SEM images at higher magnification clearly show cracks and pores on the surface. The EDS mappings of O, Ag, In, and Yb on the crack area shown in Fig. 11f reveal oxygen concentrates on the crack area, where Yb is also rich, but Ag and In are deficient. This suggests the oxidation starts at Yb sites and the formation of Yb oxide may push Ag and In to the rim of the oxidized area. Thus, we believe, the formation of Yb oxides on the sample surface could at the end destroy the quasicrystalline structure and cause the precipitation of Ag and/or In-containing metallic phases and therefore, leads to the reduction of the low-T resistivity in the aged samples.

We have also tried to prepare (AgIn)-containing other rare-earth elements, but we found single-phased QCs are hard to be made. In addition, the magnetic susceptibility of Ag-In-Yb was also measured; their magnitude at 4.2 K is very small and was found to result from the contribution of Yb impurity.4

IV. Conclusions
1. For Ag-In-Yb QCs, the resistivity decreases with increasing Yb concentration; for (AgIn)_{42.25-x}Mg_{x}Yb_{15.5}QCs, increasing Mg content enhances the value of the quasilattice constant, but reduces the resistivity.
2. Investigation of the sample surface by means of SEM and DES- mapping of constituent elements, we found the oxidation starts at Yb sites and the formation of Yb oxides could at the end destroy the quasicrystalline structure and cause the precipitation of Ag and/or In-containing metallic phases; this, we believe, the main reason to cause the decrease of low-T resistivity in the sample aged in the air.

Acknowledgments

We thank the National Science Council of the Republic of China for the financial support.
References

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Figures captions

Fig. 1. The normalized resistivity $\rho (T)/\rho (300 \text{ K})$ as a function of temperature for (a) (AgIn)$_{42.5}$Yb$_{15}$, (AgIn)$_{42.25}$Yb$_{15.5}$ and (AgIn)$_{42}$Yb$_{16}$ QCs.

Fig. 2. The resistivity vs temperature for Ag$_{42.61}$In$_{42.46}$Yb$_{14.9}$ (Fu51), Ag$_{41.95}$In$_{42.57}$Yb$_{15.48}$ (Fu87), and Ag$_{42.02}$In$_{41.99}$Yb$_{15.99}$ QCs (Don 27).

Fig. 3. The normalized resistivity $\rho (T)/\rho (300 \text{ K})$ as a function of temperature for (AgIn)$_{42.25}$Mg$_x$Yb$_{15.5}$ QCs prepared both in a arc furnace and in an induction furnace.

Fig. 4. The x-ray diffraction spectra for (AgIn)$_{42.25}$Mg$_x$Yb$_{15.5}$ QCs prepared in an induction furnace (a) $x = 2.5$ (b) $x = 5.5$ (c) $x = 8.5$ (d) $x = 10.5$.

Fig. 5. The quasilattice constant vs Mg content for (AgIn)$_{42.25}$Mg$_x$Yb$_{15.5}$ QCs prepared in an induction furnace.

Fig. 6. The normalized resistivity $\rho (T)/\rho (300 \text{ K})$ as a function of temperature for fresh and aged Fu 53a and Fu53-1 QCs.

Fig. 7. EDS mappings of O, Ag, In, and Yb in the fresh Fu 53-1 QC.

Fig. 8. EDS mappings of O, Ag, In, and Yb in the fresh Fu 53a QC.

Fig. 9. SEM images of the aged Fu 53a (a) the aged Fu 53-1(b) and the fresh Fu 53-1 QC (c).

Fig. 10. SEM images of the aged Fu 53-1 QC at different magnifications (a) 200 (b) 500 (c) 1000 (d) 2000 (e) 5000 (f) 10000.

Fig. 11. EDS mappings of O, Ag, In, and Yb in the age Fu 53-1 QC.
Fig. 1.
Fig. 2.
Fig. 3.

(a) $\rho(T)/\rho(300\text{K})$ for various compositions of $(\text{AgIn})_{42.25}\text{Mg}_x\text{Yb}_{15.5}$ + $\text{AI}_x\text{Yb}_{12}$, with $x=2.5, 5.5, 8.5, 10.5$.

(b) $\rho(T)/\rho(300\text{K})$ for various compositions of $(\text{AgIn})_{42.25}\text{Mg}_x\text{Yb}_{15.5}$ + $\text{CK}_x$, with $x=2.5, 5.5, 8.5, 10.5$. 

Fig. 3.
Fig. 4.
Fig. 5.
$\rho(T)/\rho(300{\text{K}})$ vs $T$ (K)

(a) $\text{Ag}_{42.5}\text{In}_{42.5}\text{Yb}_{15}$ [Fu53-1]
- Fresh sample; Ratio=1.097
- Aged for 150 days; Ratio=1.094

(b) $\text{Ag}_{42.5}\text{In}_{42.5}\text{Yb}_{15}$ [Fu53-1]
- Fresh sample; Ratio=1.106
- Aged for 100 days; Ratio=1.098

Fig. 6.
Fig. 7.
Fig. 8.
Fig. 9.
Fig. 10.
Fig. 11.