### Title

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NMR Studies on Icosahedral and Crystalline Phases in $\text{Al}_{67}\text{Cu}_{20}\text{Mn}_{13}$ Alloys

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Synopsis

The $^{27}\text{Al}$, $^{65}\text{Cu}$ and $^{55}\text{Mn}$ NMR spectra have been investigated in the icosahedral and crystalline phases of the $\text{Al}_{67}\text{Cu}_{20}\text{Mn}_{13}$ alloy. An as-quenched icosahedral phase transforms to a crystalline phase by heat treatment. Different peak shifts of $^{27}\text{Al}$ and $^{55}\text{Mn}$ except $^{65}\text{Cu}$ between those phases have been found. It is suggested that there are Mn atoms carrying magnetic moment and that there is and no difference in the electronic structure of Cu atoms between those phases.

I. Introduction

Since the discovery of an icosahedral quasicrystalline phase (i-phase) in rapidly quenched alloys of Al-Mn$^{1)}$, a number of alloys have been reported to have a quasicrystalline structure. $^{2,3,4)}$ However, most of them often have a low degree of quasicrystallinity resulting from the existence of a second phase and/or a high density of phason defects. Therefore, the exact structure and the atom location for the quasicrystalline phase and any subsequently discovered decagonal phase (d-phase) are still obscure. On the other hand, interesting characteristics for electronic properties in the quasicrystalline alloys have been revealed; high electric resistivity, small specific heat coefficient at low temperature$^{5)}$ and strong Curie-Weiss paramagnetism in some quasicrystalline alloys whereas the equilibrium crystalline phase exhibits only weak, temperature-independent paramagnetism$^{6)}$. There are also reports in which ferromagnetism

*The 1883th report of Institute for Materials Research
and a spin glass phase appeared\(^7,8,9\).

To help understand the local structure and the electronic properties, we have undertaken a systematic study of the quasicrystal using the pulsed NMR technique. There have been several NMR studies on the i-phase and related crystalline phases in Al-Mn alloys\(^{10,11,12}\). It has been demonstrated that the line width of Al spectra in the i-phase is much greater than in the crystalline phase. The atom sits in a broad distribution of site of relatively low symmetry. This fact has led to the suggestion that a high degree of atomic disorder is an intrinsic property of the i-phase.

Recently, new and stable single quasicrystalline Al-Cu-Tm alloys (Tm: Ni, Co, Fe, Mn, Cr and V) have been found by Tsai et al.\(^{13,14}\). Moreover, they found that the transformation of an as-quenched i-phase to a crystalline phase (c-phase) occurred by heat treatment in the Al\(_{67}\)Cu\(_{20}\)Mn\(_{13}\) alloy\(^{15}\). Here we present the NMR measurement of 27Al, 65Cu and 55Mn in the i- and c-phases in Al\(_{67}\)Cu\(_{20}\)Mn\(_{13}\) alloy\(^{16}\). In particular, we find distinct difference in the line shape and peak shift of NMR spectra among the those phases in the same constituent alloy.

II. Experimental

The specimens used in the present work were Al\(_{67}\)Cu\(_{20}\)Mn\(_{13}\) ternary alloys. A mixture of pure metals was melted in an argon atmosphere using an arc furnace. Rapidly solidified samples with a cross section of about 0.02x1mm were prepared from pre-alloyed ingots using a single roller melt spinning apparatus. The details of the preparation procedure have already been described in ref. 14. The rapidly solidified i-phase Al\(_{67}\)Cu\(_{20}\)Mn\(_{13}\) sample changed into the c phase by annealing at 500°C for 12h in vacuum. X-ray diffraction patterns with a Cu target are shown in Fig.1 for the Al\(_{67}\)Cu\(_{20}\)Mn\(_{13}\). Although the structure is different, some similarity in intensity distribution still can be observed. Indeed, the crystalline phase is a Penrose-tiling approximant of a decagonal phase, which is described by a rational sequence of 3/2 replacing the irrational one of \(r = 1 + \sqrt{5}/2 \approx 1.618\) in the quasicrystal. The structure of the Al\(_{67}\)Cu\(_{20}\)Mn\(_{13}\) approximant is an orthorhombic crystalline phase with lattice parameters of \(a = 1.48\) nm, \(b = 1.26\) nm and \(c = 1.24\) nm.

A phase-coherent type NMR apparatus with a box-car integrator for the signal average was used for the observation of spin-echo signals in the powdered form of the alloys. The NMR spectrum has been obtained by recording the integrated echo intensities as the external field was swept at a fixed frequency.
Fig. 1 X-ray powder diffractometer traces of the Al₆₇Cu₂₀Mn₁₃ quasicrystal taken with Cu Kα radiation: upper, the rapidly solidified phase and lower, the c-phase obtained after heat treatment at 500°C for 12h. Small amount of the i-phase remains.

Two sweep ranges were used: 1) by changing the current through superconducting magnetic coils (referred to as the wide range) and 2) by changing the current through the modulation coils in the persistent current mode of the superconducting magnet, (referred to as the narrow range).

The NMR measurement was made at a constant rf pulse separation in the temperature range between 5K and room temperature.

III. Result

Figure 2 shows NMR spectra observed at 5K and 100K in the i- and c-phases of Al₆₇Cu₂₀Mn₁₃ alloy while sweeping magnetic field in the wide range. Resonance signals from all constituent atom nuclei are exhibited. A general feature of ²⁷Al spectra is a relatively narrow central line superimposed on a weak and broad symmetric line, but the ratio of the intensity of the narrow to the broad component changes with temperature. Line spectra near the peak of the ²⁷Al spectra obtained at a fixed frequency while sweeping magnetic field in the narrow range are exhibited for the i- and c-phases in the Al₆₇Cu₂₀Mn₁₃ al-
Fig. 2 Spin-echo spectra for the i- and c-phases of Al$_{67}$Cu$_{20}$Mn$_{13}$ quasicrystal measured at 32.5MHz at different temperature.

loy (Fig. 3). The line shape in the i-phase becomes gradually broader with decreasing temperature while that in the c-phase becomes broader only at a temperature lower than 100K. A little broadening in line shape of $^{55}$Mn in the i-phase is seen with decreasing temperature whereas that in the c-phase is obscure (Fig. 4). However, the width of $^{55}$Mn spectra is broader in the c-phase than that in the i-phase. On the other hand, broadening of $^{65}$Cu spectra with the decrease of temperature is obscure because the superimposed broad component of $^{27}$Al spectrum increases (Fig. 5). Values of the knight shift are summarized in Table 1.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Al$<em>{67}$Cu$</em>{20}$Mn$_{13}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>i-phase</td>
</tr>
<tr>
<td>Al-27</td>
<td>0.062</td>
</tr>
<tr>
<td>Cu-65</td>
<td>0.001</td>
</tr>
<tr>
<td>Mn-55</td>
<td>0.383</td>
</tr>
</tbody>
</table>
Fig. 3 ²⁷Al spin-echo spectra measured at a fixed frequency of 39.620 MHz with sweeping magnetic field in the narrow range. Magnetic field yield by the superconducting magnet is indicated in the figure. a) i-phase and b) c-phase.
Fig. 4 $^{55}\text{Mn}$ spin-echo spectra in two different phases (i(a) and c(b) phase) measured at a fixed frequency of 37.650 MHz with sweeping magnetic field in the narrow range.
Fig. 5 $^{65}$Cu spin echo spectra in the i-(a) and c-(b) phases measured at 43.200 MHz with sweeping magnetic field in the narrow range.
IV. Discussion

For the i-phase of the Al\textsubscript{67}Cu\textsubscript{20}Mn\textsubscript{13} quasicrystal, it has been reported that magnetic susceptibility exhibits the Curie-Weiss behavior from room temperature to 4.2 K.\textsuperscript{17} However, the present data on the Knight shift of all the nuclei is temperature-independent in both the i- and c-phases, whereas the line shape becomes broader with decreasing temperature. The cause is considered to be similar to the one in the Al-Mn and Al-Mn-Si quasicrystals. In the i-phase of Al-Mn and Al-Mn-Si quasicrystals, it has been revealed from the NMR\textsuperscript{12} and Mössbauer studies\textsuperscript{18,19,20} that the broadening of the \textsuperscript{27}Al spectra is caused not only from increasing disorder in local electric field gradient distribution but also from magnetic origin.

Negative value of the \textsuperscript{27}Al Knight shift in the Al\textsubscript{67}Cu\textsubscript{20}Mn\textsubscript{13} quasicrystal and crystalline phases may be caused from the contribution of the conduction electron polarization due to the magnetic Mn atom. The difference of the \textsuperscript{27}Al and \textsuperscript{55}Mn Knight shift between the i- and c-phase may be made by different electronic structure except Cu nuclei. Therefore, the present \textsuperscript{55}Mn NMR signal is considered to be due to Mn sites that do not contribute in the essential way to the bulk paramagnetism, that is, the remaining sites of Mn atom must carry local moment. Resonance from these remaining site can be expected to be unobservably broad or due to rapid nuclear relaxation by the localized electron spin fluctuation.\textsuperscript{12}

Therefore, broadening of \textsuperscript{27}Al-spectra in the i- and c-phases with decreasing temperature is expected to be distribution due to magnetic origin. However the little change in the width of the \textsuperscript{27}Al spectra in the c-phase with temperature suggests that magnetic susceptibility of the c-phase is much smaller than in the i-phase.\textsuperscript{11}

The broader width in the \textsuperscript{65}Cu and \textsuperscript{55}Mn spectra in the c-phase implies that Cu and Mn atoms are rather randomly distributed. On the other hand, Al and Cu atoms sit on each site in the i-phase.

From the Knight shift values in Table 1, it is noticed that the Knight shifts of each constitutuent nuclei in the Al\textsubscript{67}Cu\textsubscript{20}Mn\textsubscript{13} vary in the i and c-phases\textsuperscript{20} except Cu.

V. Conclusions

In this paper, we have reported on the \textsuperscript{27}Al, \textsuperscript{65}Cu, and \textsuperscript{55}Mn resonances in different phases of Al\textsubscript{67}Cu\textsubscript{20}Mn\textsubscript{13} alloys and compared them with each other.
Results in the i- and c-phase in the Al₇Cu₁₅Mn₁₃ alloys suggest that there are Mn atoms carrying magnetic moment in both phases with no difference in electronic structure of Cu atoms between those phases.

Acknowledgement

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Reference

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