Localized Magnetic Moments and Spin Freezing in Al-Based Amorphous, Quasicrystalline and Crystalline Approximant Phases

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Al-based amorphous and quasicrystalline alloys have been prepared by high-rate sputtering and melt-quenching, respectively. The $\text{Al}_{67}\text{Cu}_{20}\text{Mn}_{13}$ crystalline approximant phase also has been made by annealing the quasicrystalline counterpart. The formation of the localized magnetic moments of 3d metals in the Al matrix is difficult except for Mn. The ratio of the magnetic Mn atoms estimated from the saturation magnetization and the Curie constant in the quasicrystalline phase is smaller than that in the amorphous phase. In the crystalline approximant phase, the ratio is comparable to that in the amorphous phase, but the average magnetic moment of magnetic Mn atoms is much smaller than that in the amorphous and quasicrystalline phases. The ratio of magnetic Mn atoms and their average magnetic moments are significantly affected by other solute atoms.

The spin glass behavior has been confirmed in the three alloy systems; $\text{Al}_{100-x}\text{Mn}_x$, $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ and $\text{Al}_{85-x}\text{Pd}_{15}\text{Mn}_x$, in both amorphous and quasicrystalline phases. The spin freezing in the latter two alloy systems occurs in a more dilute concentration range than that in the $\text{Al}_{100-x}\text{Mn}_x$ alloy system. The magnetization of the $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ and $\text{Al}_{85-x}\text{Pd}_{15}\text{Mn}_x$ alloy systems in the amorphous state is larger than in the quasicrystalline state and the spin freezing temperature in the former state is higher than that in the latter one.

From these results, it is concluded that the magnetic properties of Al-base alloys are quite sensitive to the kind of solute atoms and the phase structure.

(Received November 6, 1992)

Keywords: quasicrystal, approximant, localized magnetic moment, spin glass, giant magnetic moment

I. Introduction

Various Al-based quasicrystals and their crystalline approximant have been developed during several years. Many of these alloys consisted of magnetic transition metals and noble metals. The formation of the localized magnetic moment in the Al matrix has been of interest in the dilute alloy systems⁽¹⁾. When 3d transition metals are introduced into Al, no evidence is found for the existence of localized magnetic moments in very dilute concentration ranges. On the other hand, almost all the Al-based quasicrystalline alloys contain 3d transition metals above 10%. Therefore, the magnetic investigation would be interested in connection with the existence of the localized magnetic moment in Al in such a high concentration range. It has been well known that the formation of the localized magnetic moments in Cu and Pd is easier than in Al. The existence of the localized magnetic moment depends on the position of the d-level, the width of the bound state and the intra-atomic Coulomb potential. Especially, the density of state for Pd is high at the Fermi level and the exchange enhancement is remarkable, resulting in a giant magnetic moment.

Many Al-based icosahedral quasicrystalline alloys contain Cu or Pd of 10–20%⁽²⁾⁽³⁾, and the forming ability of the localized magnetic moment is expected to depend on the alloy systems. Furthermore, the magnetic properties of 3d transition metal alloys and compounds are remarkably affected by the local environments, namely,

the atomic distance and the coordination number⁽⁴⁾. Therefore, the magnetic properties are closely correlated with the atomic structures, suggesting the distinction among the amorphous, quasicrystalline and crystalline approximant phases.

In the present paper, mainly, the magnetic properties of icosahedral quasicrystalline alloys have been investigated. At first, the existence of the localized magnetic moment is discussed. Next, the effective magnetic moment, the ratio of magnetic Mn atoms and the spin glass behavior for Al-based ternary alloys containing Mn are presented and compared with those for $\text{Al}_{100-x}\text{Mn}_x$ binary alloys. The change of the magnetic properties due to the partial substitution of Mn by Cr is also discussed. Finally, the difference in the magnetic properties of $\text{Al}_{67}\text{Cu}_{20}\text{Mn}_{13}$ alloys among the amorphous, quasicrystalline and crystalline approximant phases is presented because their comparison is informative for the structural study on the quasicrystalline alloys.

II. Experimental

Alloying was made by arc-melting in an argon atmosphere using starting materials of Al of 99.99 mass% and transition metals of 99.9 mass% purity. The melting was repeated five times. Various kinds of Al-based amorphous and quasicrystalline alloys were prepared by high-rate sputtering and melt quenching, respectively. $\text{Al}_{67}\text{Cu}_{20}\text{Mn}_{13}$ crystalline approximant was made by an-

nealing the quasicrystalline counterpart at 770 K for 12 h. Their amorphous, quasicrystalline and crystalline states were confirmed by X-ray diffraction using Mo- K_α radiation. The former state was also identified by electron diffraction patterns. The alloy compositions of the sputtered samples were analyzed by spectrophotometry and titration methods.

The magnetization up to 4.5×10^6 A/m at 4.2 K, the temperature dependence of susceptibility and the magnetic cooling effect were measured with a SQUID magnetometer. The magnetization was also measured at 4.2 K in the pulsed magnetic fields up to 3×10^7 A/m with a duration of 13 ms. The temperature dependence of AC susceptibility was obtained by a mutual induction method in 796 A/m with a frequency of 80 Hz.

III. Results and Discussion

Figure 1 shows the magnetization curves up to 3×10^7 A/m at 4.2 K for Al-base amorphous alloys containing almost the same composition of Mn. These data exhibit a remarkable curvature, being suggestive of the existence of the localized magnetic moment. $\text{Al}_{70}\text{Pd}_{15}\text{Mn}_{15}$ has the largest magnetization, but $\text{Al}_{84.8}\text{Mn}_{15.2}$ oppositely exhibits the smallest value.

The magnetic susceptibility of $\text{Al}_{65}\text{Cu}_{20}\text{Mn}_{15}$ and $\text{Al}_{70}\text{Pd}_{15}\text{Mn}_{15}$ quasicrystalline (Q) alloys exhibits a Curie-Weiss type temperature dependence in wide temperature ranges as shown in Fig. 2. No other quasicrystalline alloys containing other transition metals such as Al-Cu-Co and Al-Pd-Co show a remarkable temperature dependence⁽⁵⁾. In the amorphous state, $\text{Al}_{85-x}\text{Pd}_{15}\text{Mn}_x$, $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ and $\text{Al}_{100-x}\text{Mn}_x$ alloys also show a striking temperature dependence in a similar manner as given in Fig. 2.

The effective magnetic moment is deduced from the Curie constant given by the following equation:

$$\chi - \chi_0 = C / (T - \theta_p), \quad (1)$$

where χ_0 and θ_p are the temperature independent susceptibility and the paramagnetic Curie temperature, respectively. Figure 3 shows the concentration dependence of the effective magnetic moment P_{eff} deduced from eq. (1)

Fig. 1 Magnetization curves up to 3×10^7 A/m at 4.2 K for $\text{Al}_{70}\text{Pd}_{15}\text{Mn}_{15}$, $\text{Al}_{65}\text{Cu}_{20}\text{Mn}_{15}$ and $\text{Al}_{84.8}\text{Mn}_{15.2}$ amorphous alloys.

Fig. 2 Temperature dependence of magnetic susceptibility of $\text{Al}_{70}\text{Pd}_{15}\text{Mn}_{15}$ and $\text{Al}_{65}\text{Cu}_{20}\text{Mn}_{15}$ quasicrystalline (Q) alloys.

Fig. 3 Concentration dependence of the effective magnetic moment of $\text{Al}_{100-x}\text{Mn}_x$, $\text{Al}_{85-x}\text{Pd}_{15}\text{Mn}_x$ and $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ alloys in the amorphous (A) and quasicrystalline (Q) states.

for three alloy systems in the amorphous (A) and quasicrystalline (Q) states. Comparing with the same magnitude of P_{eff} , the composition of Mn for $\text{Al}_{100-x}\text{Mn}_x$ is much higher than that for the other two alloy systems, suggesting that the formation of the localized magnetic moment in $\text{Al}_{100-x}\text{Mn}_x$ is much difficult than in the latter systems. The concentration dependence of P_{eff} of $\text{Al}_{100-x}\text{Mn}_x$ in the amorphous (A) and quasicrystalline (Q) states is almost the same each other. However, the difference between the amorphous (A) and quasicrystalline (Q) states for the $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ alloys[†] is distinct. The $\text{Al}_{70}\text{Pd}_{15}\text{Mn}_{15}$ alloy also shows a remarkable difference between the amorphous (▼) and quasicrystalline (▽) states. This comes from that the latter two alloy systems contain Cu or Pd in which the localized magnetic moment is easily established. From these results, it is concluded that there is remarkable difference in the magnetic properties between the amorphous and quasicrystalline alloys, reflecting their structural difference. In the case of $\text{Al}_{100-x}\text{Mn}_x$, the difference is not so apparent because of difficulty of the formation of the

[†] Previous data on $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ quasicrystalline alloys⁽⁵⁾⁽⁶⁾ should be replaced by the present results.

Fig. 4 Magnetization against the reciprocal magnetic field curve of $\text{Al}_{67}\text{Cu}_{20}\text{Mn}_{13}$ quasicrystalline (Q) alloy, together with that of Cu-Mn crystalline dilute alloy⁽⁹⁾.

Fig. 5 Concentration dependence of the saturation magnetization of $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ in the amorphous (A) and quasicrystalline (Q) states and $\text{Al}_{85-x}\text{Pd}_{15}\text{Mn}_x$ in the quasicrystalline (Q) states.

localized magnetic moment as mentioned before.

It has been pointed out that the magnetization is much smaller than the value expected from the effective magnetic moment⁽⁷⁾. This means that the magnitude of magnetic moment is not uniform, depending on the Mn sites in the quasicrystalline phase. From various experiments, it has been confirmed that there are magnetic and non-magnetic Mn atoms⁽⁸⁾⁻⁽¹⁰⁾. In order to compare the saturation magnetization, M_s , with the value expected from the effective magnetic moment, the high field measurements are required because the strength of the present field given in Fig. 1 is not enough to determine

the saturation magnetization. However, by assuming the $1/H$ dependence, the M_s value of the Al-Mn-Si quasicrystalline alloy has been estimated by scaling with the data on CuMn crystalline dilute alloys⁽¹⁰⁾. In the same way, Fig. 4 shows the representative $1/H$ plot for $\text{Al}_{67}\text{Cu}_{20}\text{Mn}_{13}$ quasicrystalline (Q) alloy, together with that of CuMn crystalline dilute alloys⁽¹⁰⁾. The scaling seems to work well over a wide range of the magnetic field. The concentration dependence of the saturation magnetization per Mn atom thus obtained for the $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ amorphous (A) and quasicrystalline (Q) alloys is given in Fig. 5, together with that for the $\text{Al}_{85-x}\text{Pd}_{15}\text{Mn}_x$ quasicrystalline (Q) alloys. These values are much smaller than the values expected from the effective magnetic moments in a similar manner to the $\text{Al}_{100-x}\text{Mn}_x$ alloy system⁽⁷⁾.

The magnetic properties of transition metal alloys are sensitive to the local structure. Especially, the magnitude of the magnetic moment of Mn in various alloys and compounds is satisfactorily explained by the Pauling valence⁽⁴⁾⁽¹¹⁾. According to this model, the magnetic properties are dominantly governed by the coordination number and the atomic distance. Therefore, the magnitude of magnetic moment does not necessarily correspond to the concentration. For example, the effective magnetic moment of $\delta\text{-Al}_{11}\text{Mn}_4$ is much smaller than that of $\Phi\text{-Al}_{10}\text{Mn}_3$ ⁽¹²⁾. The atomic sites of the Mn atoms in the quasicrystalline structure is not definitive, although the structure investigations are carried out intensively. It is considered that the local structure of the surrounding Mn atoms is also not uniform in the amorphous state. The magnetic inhomogeneity would, therefore, occur in the amorphous state as well as in the quasicrystalline and crystalline states. The ratio of magnetic Mn atoms, X_m/X , is correlated with the following expression⁽¹⁰⁾:

$$M_s(M_s X / X_m + 2\mu_B) = 3k_B C / N, \quad (2)$$

where M_s and N are the saturation magnetization per Mn atom and the number of Mn atoms, respectively. The g -value is assumed to be 2.0 and k_B is the Boltzmann constant. The concentration dependence of the ratio of magnetic Mn atoms for the three alloy systems is presented in Fig. 6. The ratios in the amorphous state of $\text{Al}_{70}\text{Pd}_{15}\text{Mn}_{15}$ and $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ are about twice those in the quasicrystalline state. But, no remarkable difference is observed between the two states in $\text{Al}_{100-x}\text{Mn}_x$. Since the formation of the localized magnetic moment is not easy in the Al matrix, the magnetic properties of the $\text{Al}_{100-x}\text{Mn}_x$ alloys would be insensitive to the structural change. In the figure, the line above 20% is given by the dotted line because these alloys contains a decagonal phase above this concentration⁽¹³⁾. Figure 7 shows the concentration dependence of the mean value of the magnetic moment of magnetic Mn atoms, P_c , calculated from eq. (2). Compared with the data on $\text{Al}_{100-x}\text{Mn}_x$, relatively large values of P_c for the $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ and $\text{Al}_{70}\text{Pd}_{15}\text{Mn}_{15}$ alloy systems are obtained in lower concentration ranges. The icosahedral quasicrystalline alloys are classified into two categories, that is, the Al-Mn and F

Fig. 6 Concentration dependence of the ratio of magnetic Mn atoms in $\text{Al}_{100-x}\text{Mn}_x$, $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ and $\text{Al}_{70}\text{Pd}_{15}\text{Mn}_{15}$ alloys in the amorphous (A) and quasicrystalline (Q) states.

Fig. 7 Concentration dependence of the average magnetic moment of magnetic Mn atoms for $\text{Al}_{100-x}\text{Mn}_x$, $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ and $\text{Al}_{85-x}\text{Pd}_{15}\text{Mn}_x$ alloys in the amorphous (A) and quasicrystalline (Q) states.

types. It is considered that the structure difference between them is the existence of long range order and that the local structure is very similar to each other⁽¹⁴⁾. Therefore, the difference in the magnetic properties between $\text{Al}_{100-x}\text{Mn}_x$ and $\text{Al}_{85-x}\text{Pd}_{15}\text{Mn}_x$, $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ would be mainly caused by the partial substitution of Cu or Pd for Mn because these elements help to produce the localized magnetic moment. Both the ratio, X_m/X , and the mean value, P_c , of $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ quasicrystalline (Q) alloys are about half those of the amorphous (A) counterparts. In the case of the $\text{Al}_{85-x}\text{Pd}_{15}\text{Mn}_x$ quasicrystalline alloys, the ratio shows a similar tendency to that of the $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ alloys and the mean value exceeds the bare Mn moment of $5\mu_B$. Therefore, it is concluded that this alloy system has a giant magnetic moment in a similar manner to that in dilute crystalline alloys. Such a giant magnetic moment in Pd dilute alloys is induced by spin polarization of the conduction electrons. In the crystalline state, PdCo, PdFe and PdMn dilute alloys have a giant magnetic moment, but Al-Pd-Co, Al-Pd-Fe quasicrystalline alloys carry no large magnetic moment⁽⁵⁾. Consequently, only Mn atoms in

Fig. 8 AC magnetic susceptibility curves measured in 796 A/m with 80 Hz for $\text{Al}_{66}\text{Cu}_{20}\text{Mn}_{14}$ alloys in the amorphous and quasicrystalline states.

Fig. 9 Concentration dependence of the spin freezing temperature T_f for $\text{Al}_{100-x}\text{Mn}_x$, $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ and $\text{Al}_{85-x}\text{Pd}_{15}\text{Mn}_x$ alloys in the amorphous (A) and quasicrystalline (Q) states.

Al-Pd-Mn alloys have a giant magnetic moment.

The concentration of Mn in the present alloys exceeds 10%, but the ratio of magnetic Mn atoms is very small as shown in Fig. 6. Then, they are regarded as magnetically much dilute alloys. The spin glass state is often set up by the frustrated spins due to the oscillating RKKY interaction in magnetically dilute alloys⁽¹⁵⁾. Figure 8 shows the temperature dependence of the AC susceptibility measured in 796 A/m (= 10 Oe) with the frequency of 80 Hz for the $\text{Al}_{66}\text{Cu}_{20}\text{Mn}_{14}$ alloys in the quasicrystalline and amorphous states. They exhibit a characteristic cusp of spin glasses. The magnetic cooling effect measured in 2388 A/m (= 30 Oe) for those alloys also exhibits a clear hysteresis between the zero-field and field coolings. The spin freezing temperature corresponds to the temperature where the AC susceptibility curves show a cusp. From these results, these two alloys are spin glasses in low temperature ranges. The other two alloy systems also exhibit a similar spin glass behavior⁽⁵⁾⁽¹⁶⁾. Figure 9 shows the concentration dependence of the spin freezing temperature T_f of these three alloy systems in the amorphous and quasicrystalline states. The $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ and

Fig. 10 Magnetization curves up to 4.5×10^6 A/m at 4.2 K for $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10-x}\text{Cr}_x$ quasicrystalline (Q) alloys.

Fig. 11 Concentration dependences of the ratio of the magnetic Mn atoms, X_m/X , and their average magnetic moment, P_c , for $\text{Al}_{65}\text{Cu}_{20}\text{Mn}_{15-x}\text{Cr}_x$ and $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10-x}\text{Cr}_x$ quasicrystalline (Q) alloys.

$\text{Al}_{85-x}\text{Pd}_{15}\text{Mn}_x$ alloy systems show the spin glass behavior in a much lower Mn concentration range compared with that of the Al-Mn alloy system. Furthermore, the spin freezing temperature T_f of the $\text{Al}_{85-x}\text{Pd}_{15}\text{Mn}_x$ alloys is higher than that of the $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ alloys.

The magnetic properties of quasicrystalline alloys are drastically affected by substituting Mn by small amounts of other 3d transition metals. In the present study, Mn is replaced by Cr which has no magnetic moment in Al. Figure 10 shows the magnetization curves of the

Table 1 The ratio of the magnetic Mn atoms, X_m/X , and their average magnetic moment P_c for $\text{Al}_{67}\text{Cu}_{20}\text{Mn}_{13}$ alloys in the amorphous, quasicrystalline and crystalline approximant states.

$\text{Al}_{67}\text{Cu}_{20}\text{Mn}_{13}$	$X_m/X(\%)$	P_c/μ_B	T_f/K
Quasicrystalline	9	1.8	~ 2
Amorphous	16	3.3	3.5
Approximant	18	0.5	—

Fig. 12 Magnetization curves up to 4.5×10^6 A/m at 4.2 K for $\text{Al}_{67}\text{Cu}_{20}\text{Mn}_{13}$ alloys in the amorphous, quasicrystalline and crystalline approximant states.

$\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10-x}\text{Cr}_x$ quasicrystalline (Q) alloys. The magnitude of magnetization decreases remarkably with increasing Cr content. We can estimate the ratio of magnetic Mn atoms and the mean value of the magnetic moment in a similar manner as described on Figs. 6 and 7. Figure 11 shows the ratio X_m/X and P_c for $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10-x}\text{Cr}_x$ and $\text{Al}_{65}\text{Cu}_{20}\text{Mn}_{15-x}\text{Cr}_x$ quasicrystalline alloys. From this figure, the ratio increases but the mean value of the magnetic moment decreases with increasing Cr content in both alloy systems. It should be noted that the ratio in the $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ quasicrystalline alloys slightly decreases with decreasing Mn content as seen Fig. 6.

In the investigations of structures of quasicrystalline alloys, particular attention is called to their approximants⁽¹⁷⁾. A remarkable difference in the magnetic properties is expected because they are sensitive to the environments as mentioned before. Figure 12 shows the magnetization curves of $\text{Al}_{67}\text{Cu}_{20}\text{Mn}_{13}$ alloys in the different three states. The structure of crystalline approximant has been identified as an Al_3Mn type orthorhombic structure⁽¹⁸⁾. The detailed analysis of the relation between

the structure and magnetic properties is now in progress. The magnetization decreases in the sequence: amorphous $\rightarrow$ quasicrystalline $\rightarrow$ approximant phase. Drastic decrease in the magnetization after crystallization of quasicrystalline alloys has been also observed in the $\text{Al}_{100-x}\text{Mn}_x$ alloy system⁽¹⁹⁾. These three alloys also show a Curie-Weiss type temperature dependence, then, they are treated in the same way as the data in Figs. 6 and 7. The ratio of magnetic Mn atoms, X_m/X , and their mean value of magnetic moment, P_c , are given in Table 1, together with the spin freezing temperature, T_f . The ratio for the crystalline approximant is very similar to that of amorphous alloy, but the magnetic moment is extremely small, reflecting the small magnetization as seen from Fig. 12. The similarity of the ratio between the amorphous and approximant states may be fortuitous because the magnetic properties are very sensitive to the local structure as mentioned before. It should be emphasized that the ratio of the quasicrystalline alloy is about half, compared with the other two alloys. The spin glass behavior is observed in the amorphous state because of the large magnetic moment. The freezing temperature of the quasicrystalline alloy is linearly extrapolated from the concentration dependence (see Fig. 9).

IV. Conclusion

The magnetic properties of three kinds of Al-based quasicrystalline and amorphous alloys have been discussed. Furthermore, the change of the magnetic properties by replacing Mn by small amounts of other 3d transition metals and the difference among the amorphous, quasicrystalline and crystalline approximants of $\text{Al}_{67}\text{Cu}_{20}\text{Mn}_{13}$ alloys are presented. The many different magnetic properties have been confirmed, and the main results are summarized as follows:

- (1) The existence of localized magnetic moment is clear for $\text{Al}_{100-x}\text{Mn}_x$, $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ and $\text{Al}_{85-x}\text{Pd}_{15}\text{Mn}_x$ alloys in both of the amorphous and quasicrystalline states.
- (2) The estimated saturation magnetization is much smaller than the value expected from the effective magnetic moment, suggesting the non-uniformity of the magnetic state of Mn.
- (3) The ratio of the magnetic Mn atoms in $\text{Al}_{85-x}\text{Pd}_{15}\text{Mn}_x$ and $\text{Al}_{80-x}\text{Cu}_{20}\text{Mn}_x$ quasicrystalline alloys is about half that of the amorphous counterparts.
- (4) The formation of a giant magnetic moment is confirmed in $\text{Al}_{85-x}\text{Pd}_{15}\text{Mn}_x$ alloys.

(5) Three alloy systems are magnetically dilute and accompanied by the spin glass behavior.

(6) The effect on the magnetic properties is remarkable when small amounts of Mn are replaced by Cr.

(7) The magnetization of the crystalline approximant phase of $\text{Al}_{67}\text{Cu}_{20}\text{Mn}_{13}$ is much smaller than that of the amorphous counterpart, although the ratio of magnetic Mn atoms is comparable with each other.

Acknowledgment

The present study has been supported by the Special Coordination Funds for Promoting Science and Technology Agency of the Japanese Government. The authors are indebted to Dr. A. P. Tsai of Institute for materials Research, Tohoku University, for supplying the $\text{Al}_{67}\text{Cu}_{20}\text{Mn}_{13}$ alloy.

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