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Electronic properties of stable icosahedral alloys

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We report specific-heat and resistivity results on icosahedral (*i*) Ga-Mg-Zn, Al-Cu-Fe, and Al-Cu-V alloys. The electronic densities of states at the Fermi level obtained for the stable *i* phases of Ga-Mg-Zn and Al-Cu-Fe are substantially less than those found in metastable *i* phases (Al-Cu-V, Al-Cu-Mg, and Al-Mg-Zn), as small as one-sixth of their free-electron values. Implications for the structural stability of *i* phases will be discussed. Magnetic-susceptibility and specific-heat measurements on Al-Cu-Fe *i* phases prepared by rapid quenching and from annealing of the conventionally cast sample show an increased magnetic behavior in the melt-spun sample with respect to the annealed sample. Also, similar to earlier results on Al-Cu-Li *i* alloys, the Debye temperature of the melt-spun sample is found to be reduced in comparison with the annealed one. These differences in physical properties are attributed to structural differences in the samples. The electronic diffusivities in the stable *i* phases of Ga-Mg-Zn and Al-Cu-Li are an order of magnitude greater than those observed in previously reported icosahedral alloys, suggesting that the transport properties of some *i* phases resemble those of crystalline, rather than glassy, alloys.

The relationship between icosahedral (*i*) symmetry and observed physical properties in alloys exhibiting this symmetry has been the subject of many experimental and theoretical investigations.[1] Different techniques, such as resistivity,[2] magnetization,[3] specific-heat,[4] and Mössbauer[5] measurements to name but a few, have been used to probe various electronic properties. While for some quasicrystalline (QC) systems the observed electronic properties can be understood in terms of conventional theories of electronic structure and transport, in others there exist substantial differences in reported properties and interpretations thereof. For example, in *i*-phase Al-Mn there exists a substantial range for reported values of resistivity (~ 150 $\mu\Omega$ cm in Ref. 2 to ~ 1000 $\mu\Omega$ cm in Ref. 6) and electronic density of states (DOS) at the Fermi energy as determined from specific-heat data (the electronic coefficient of specific heat, proportional to the DOS, ranges from 2.6 to 13 mJ/g-at. K^2 as reported in Refs. 4 and 7, respectively). The large resistivities observed in *i*-Al-Mn (~ 150 $\mu\Omega$ cm) and *i*-Pd-U-Si (~ 200 $\mu\Omega$ cm) have been attributed to scattering of conduction electrons by the presence of open *d* bands.[2] Berger *et al.* have proposed a similar argument to explain the apparent enhancement in DOS observed in Al-Mn and Al-Mn-Si quasicrystals,[7] however magnetic contributions to specific heat at low temperatures complicate the determination of DOS. In *i* phases containing only simple metals (Al-Mg-Zn, Al-Cu-Mg, and Al-Cu-Li, for example), where complications due to unfilled *d* bands are not present, resistivities are relatively small [room temperature values of 79 and 65 $\mu\Omega$ cm for Al-Mg-Zn (Ref. 8) and Al-Cu-Mg (Ref. 9), respectively] compared with those reported for *i*-Al-Mn, and the densities of states derived from specific-heat data are well described by the nearly-free-electron model. However, in the stable *i* phase of Al-Cu-Li where $\rho \simeq 95$ $\mu\Omega$ cm, the DOS is found to be just a third of its free-electron value.[9] As the variety of quasicrystalline systems grows, and with the availability of single-phase samples, a more coherent picture of the electronic properties as related to the icosahedral structure and its stability is gradually emerging.

In this paper, we present the results of specific-heat, magnetic susceptibility, and resistivity measurements on icosahedral alloys of melt-spun $Ga_{16}Mg_{32}Zn_{52}$ (Ref. 10) and $Al_{75}Cu_{15}V_{10}$ (Ref. 11), and $Al_{65}Cu_{20}Fe_{15}$ (Ref. 12) obtained by both rapid quenching and from annealing of the as-cast ingot. These samples are selected because (1) essentially single-phase icosahedral samples can be obtained; (2) *i*-$Ga_{16}Mg_{32}Zn_{52}$ and *i*-$Al_{69}Cu_{20}Fe_{15}$ are known to be stable up to melting while *i*-$Al_{75}Cu_{15}V_{10}$ is metastable with respect to its equilibrium crystalline phases, thus allowing direct observation of the relationship between the electronic and vibrational properties of the *i* phases and their stability; and (3) since *i*-$Al_{65}Cu_{20}Fe_{15}$ can be obtained by both rapid solidification and long-term annealing, the effects on the electronic, lattice, and magnetic properties due to different cooling rates can be studied. Comparison of results with theories on possible origins for the stability of the icosahedral phase will be made.

Thin ribbons of *i*-$Ga_{16}Mg_{32}Zn_{52}$, *i*-$Al_{65}Cu_{20}Fe_{15}$, and

amorphous $Al_{75}Cu_{15}V_{10}$ were obtained by melt spinning on an 8-in.-diam copper wheel with a tangential velocity of 60 m/s in a partial pressure of helium. i-$Al_{75}Cu_{15}V_{10}$ was obtained by annealing the as-spun amorphous ribbon at 547 °C for 6 min. i-$Al_{65}Cu_{20}Fe_{15}$ was obtained by an anneal of the as-cast ingot at 845 °C for 48 h. Structures of powdered icosahedral samples were examined by a Siemens x-ray diffractometer with Cu $K\alpha$ radiation. Only those samples containing more than ~95% icosahedral phase were used in our measurements. Resistivity measurements were made using the standard four-terminal method from 0.35 K to room temperature. Specific-heat measurements were performed by the relaxation method in the temperature range of 0.7 to 20 K. A more detailed discussion of the specific-heat–measuring technique has been given in Ref. 9. Both dc and ac susceptibility measurements were made. The dc measurements were performed in a SHE (Biotechnologies, Inc.) model 905 SQUID (superconducting quantum interference device) susceptometer in the temperature range of 2.2 K to room temperature, and low-temperature ac susceptibility measurements were made by the mutual induction technique in a ^{4}He probe from 1.3 to 7 K.

The results of resistivity measurements are listed in Table I. Resistivities are listed only for those alloys which measurements on several ribbons from different batches yielded reproducible values (to within 10%). Listed values are average resistivities. For the i-$Al_{65}Cu_{20}Fe_{15}$ samples, values measured were consistently high ($>1000\ \mu\Omega$ cm) with wide variations from sample to sample. Additional discussion of the transport properties will be given later. Room-temperature resistivities were 98 and 107 $\mu\Omega$ cm for i-$Ga_{16}Mg_{32}Zn_{52}$ and i-$Al_{75}Cu_{15}V_{10}$, respectively, with the temperature coefficient of resistivity for each being small and positive. $Ga_{16}Mg_{32}Zn_{52}$ exhibited a superconducting transition at $T_c=0.40$ K with a transition width of 0.02 K, while all other samples remained normal down to 0.35 K. For

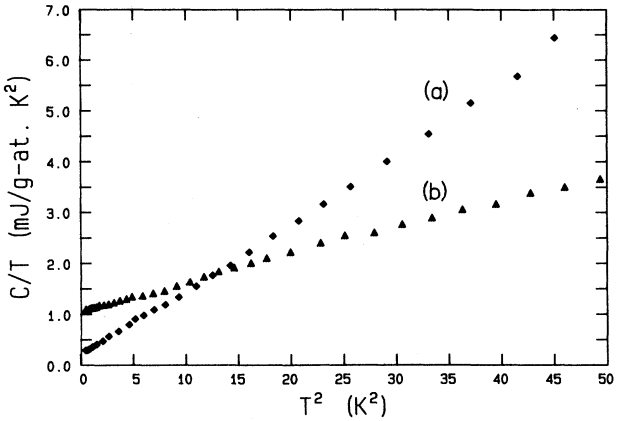

FIG. 1. C/T vs T^2 for (a) i-$Ga_{16}Mg_{32}Zn_{52}$ and (b) i-$Al_{75}Cu_{15}V_{10}$.

$Al_{75}Cu_{15}V_{10}$, which was shown to be nonmagnetic through susceptibility measurements, and $Ga_{16}Mg_{32}Zn_{52}$, the analysis of the specific-heat data was straight forward. The specific heat was assumed to be the sum of the linear electronic contribution and a cubic phonon term,

$$C=\gamma T+\beta T^3\ , \tag{1}$$

where the constants γ and β allow one to determine DOS, and the Debye temperature Θ_D, respectively. The DOS (in units of states/eV atom) is obtained from γ (in mJ/g-at. K^2) by multiplying by the factor $0.422/(1+\lambda)$, where λ is the electron-phonon coupling constant. The latter is determined following a procedure given in Ref. 9. For samples in this work, $\lambda\sim 0.2$–0.35.

As can be seen by the plot of C/T versus T^2 in Fig. 1, the data for the two nonmagnetic samples are described well by Eq. (1) over the temperature range measured.

TABLE I. Results of resistivity and specific-heat measurements. $N(0)$ is the density of states at the Fermi energy (DOS in the text) determined from γ, and $N_{FE}(0)$ is the free-electron value.

	$\rho_{300\ K}$ ($\mu\Omega$ cm)	$\frac{\rho_{4.2\ K}}{\rho_{300\ K}}$	γ (mJ/g-at. K^2)	Θ_D (K)	S_m (mJ/g-at. K)	$N(0)$ (states/eV at.)	$N_{FE}(0)$ (states/eV at.)	D (cm^2/s)
Stable i phase								
$Ga_{16}Mg_{32}Zn_{52}$	98	0.93	0.18	243		0.06	0.37	~21
$Al_{65}Cu_{20}Fe_{15}$ (annealed from as-cast)		~1.2	0.17	377	2.32	0.06	0.31	
$Al_{65}Cu_{20}Fe_{15}$ (as-spun)		~1.2	0.21	343	14.2	0.07	0.31	
$Al_{56.1}Cu_{10.2}Li_{33.7}$ (Ref. 9)	95	0.94	0.34	346		0.11	0.36	~11
Metastable i phases								
$Al_{75}Cu_{15}V_{10}$	107	0.95	1.07	337		0.38	0.34	~2.4
$Al_{52.4}Cu_{12.6}Mg_{35}$ (Ref. 9)	68	0.96	1.10	295		0.33	0.38	~5.1
$Al_{25}Zn_{37.5}Mg_{37.5}$ (Ref. 8)	79	0.97	0.92	258		0.28	0.38	~5.2

Values of γ were 0.18 and 1.07 mJ/g-at. K^2 with Θ_D of 243 and 337 K for $Ga_{16}Mg_{32}Zn_{52}$ and $Al_{75}Cu_{15}V_{10}$ respectively. This indicates the DOS of $Ga_{16}Mg_{32}Zn_{52}$ is substantially lower than (approximately a sixth of) its free-electron value while that of $Al_{75}Cu_{15}V_{10}$ is comparable.[13] Values of the DOS are listed in Table I.

The specific heat for both samples of $Al_{65}Cu_{20}Fe_{15}$ are shown in Fig. 2, along with that of $Al_{75}Cu_{15}V_{10}$ for comparison. For the as-cast sample, a small bump is observed at low temperature with a maximum around 2 K and a small deviation from the simple behavior of Eq. (1). A much larger deviation from Eq. (1) is seen for the as-spun sample of $Al_{65}Cu_{20}Fe_{15}$, and again a broad maximum in C is observed at ~ 2 K. It should be noted that a maximum in C does not necessarily correspond to a maximum in C/T (as the data are shown in Fig. 2). A spin-glass-like cusp in the ac susceptibility, shown in the inset of Fig. 3, was observed at 1.55 and 1.60 K for the as-spun and annealed $Al_{65}Cu_{20}Fe_{15}$ samples, respectively. This is typical of canonical spin-glasses behavior where the maximum in C is found at temperatures 20–40 % higher than the susceptibility cusp (Ref. 14). More about the magnetic properties of these samples will be discussed later. Similar spin-glass-like behavior has previously been observed in various other magnetic quasicrystalline compounds.[4,7] Accurate determination of the electronic and lattice terms to the specific heat is made difficult by the presence of the magnetic contribution C_m which may be quite large at low temperatures (as in the melt-spun sample) and slowly tails off at higher temperatures. Indeed, in other spin-glass systems, magnetic contributions have been detected at temperatures in excess of 5 times the susceptibility cusp temperature.[15]

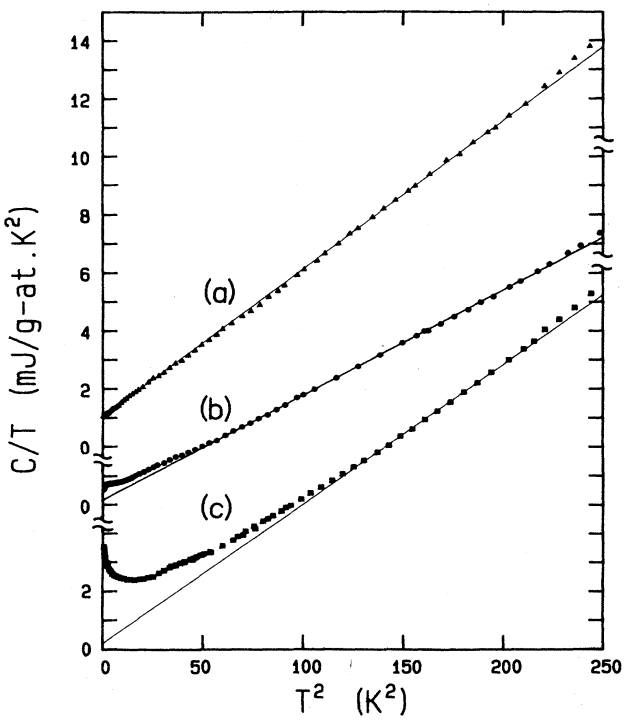

FIG. 2. C/T vs T^2 for (a) i-$Al_{75}Cu_{15}V_{10}$, (b) annealed i-$Al_{65}Cu_{20}Fe_{15}$, and (c) rapidly quenched i-$Al_{65}Cu_{20}Fe_{15}$.

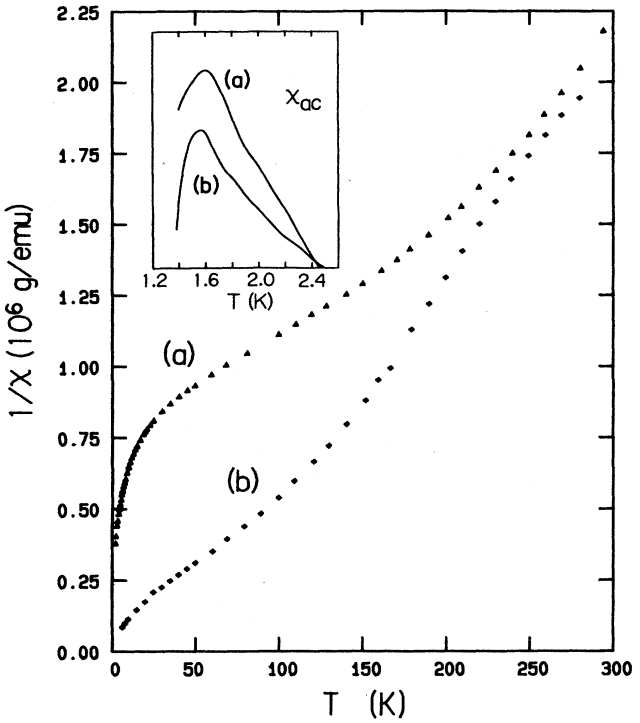

FIG. 3. dc susceptibility data, plotted as $1/\chi$ vs T, for (a) annealed i-$Al_{65}Cu_{20}Fe_{15}$, and (b) rapidly quenched i-$Al_{65}Cu_{20}Fe_{15}$. In the inset, ac susceptibility in arbitrary units.

For i-$Al_{75}Cu_{15}V_{10}$, which is nonmagnetic, the specific-heat data follow Eq. (1) up to $T \sim 14$ K, above which deviations from the simple Debye law appear. Since the composition and alloying elements for $Al_{65}Cu_{20}Fe_{15}$ and $Al_{75}Cu_{15}V_{10}$ are similar, it is expected that the phonon contribution to the specific heat in the $Al_{65}Cu_{10}Fe_{15}$ samples would follow the Debye T^3 law over a similar temperature range, provided that the Θ_D values for these samples are comparable to that of $Al_{75}Cu_{15}V_{10}$. Therefore, even in the presence of a magnetic contribution C_m which causes the distinct upturns in C/T as T^2 decreases, one may still locate a linear region of C/T versus T^2 extending over a temperature range which is then shown to be consistent with the Θ_D value. Linear regions in the range of 8 to 15 K and 10.5 to 14.5 K are obtained for the annealed and as-spun sample, respectively. A fit of Eq. (1) for the data in these regions yields values for γ of 0.17, 0.21 mJ/g-at. K^2 and Θ_D of 377, 343 K for the annealed and as-spun samples, respectively. Thus, the Θ_D values for the Al-Cu-V and Al-Cu-Fe i phases are comparable. A similar percentage ($\sim 10\%$) reduction in Θ_D of the as-spun sample with respect to the bulk sample was also observed in Al-Cu-Li i phases (Ref. 9). In view of the upward curvature in C/T at low temperature, the γ values obtained might actually have been slightly overestimated. The values of the DOS derived from the electronic terms are approximately a fifth of their estimated free-electron values.[13] DOS values are given in

Table I. For completeness, we include the DOS of i-$Al_{56.1}Cu_{10.2}Li_{33.7}$ from Ref. 9. The values of magnetic entropy $S_m = \int (C_m/T)dT$ are also listed in Table I.

The dc magnetic susceptibility, measured in a field of 5 kG, is shown in Fig. 3 as $1/\chi$ versus T for samples of $Al_{65}Cu_{20}Fe_{15}$. Attempts to fit the data to Curie-Weiss law were unsuccessful over most of the temperature range measured. Two general points, however, can be made concerning the effective moment (expressed in p_{eff} μ_B) as related to the slope of $1/\chi$ (where the slope $\propto 1/p_{\text{eff}}^2$): (1) At the highest temperature measured, both samples possess comparable moments; and (2) below 50 K the annealed sample can be seen to be rapidly losing its localized moment as evident by the divergence of the slope at lower temperatures. This magnetic difference between the two $Al_{65}Cu_{20}Fe_{15}$ samples measured is also confirmed by the magnetic entropy calculated from the specific heat, where S_m for the as-spun sample is more than seven times larger than that of the annealed. Mössbauer measurements performed on $Al_{65}Cu_{20}Fe_{15}$ samples obtained by rapid quenching and from an anneal of the as-cast sample also show magnetic differences between the samples.[16]

In this work, we have shown that the DOS of stable i phases (Al-Cu-Li, Al-Cu-Fe, and Ga-Mg-Zn) are substantially lower than their free-electron values. A plausible interpretation of these results can be made as follows. In previous studies,[13,17,18] there have been attempts to understand the formation and stability of the i phase in different alloys in terms of Hume-Rothery rules, which were originally developed to explain the dependence of structure on the electron concentration in noble metal alloys.[19] It has been proposed[20] that stability of an alloy can occur when the free-electron-like Fermi sphere of the valence electrons just touches the Brillouin-zone boundaries for a given structure, given rise to Van Hove–type singularities in the DOS. A particular phase will be stabilized as a result of a reduction in energy when the Fermi level lies at a minimum in the DOS. Therefore it is favorable for a stable i phase to form when its Fermi wave vectors almost coincide with the positions of strong peaks in the structure factor.[13,18] The unusual stability of the icosahedral phases studied here and the observed low DOS at the Fermi level appears to be consistent with this picture. Further studies are underway to probe the electronic structure in the region of i phase stability.

Resistivities reported for the initial icosahedral alloys of Al-Mn and Pd-U-Si (Ref. 2) were quite large (>150 $\mu\Omega$ cm) with corresponding electronic diffusivity $D<2$ cm^2/s. Here, D is defined as $v_F l/3$ where v_F is the Fermi velocity and l is the electric mean free paths. These D values then yield electronic mean free paths on the order of interatomic spacings, comparable to those observed in metallic glasses. Attention was then focused on i phases containing only simple metals, as in Al-Mg-Zn (Ref. 8) and Al-Cu-Mg (Refs. 9 and 21). For these materials where the DOS is free-electron-like, values of $D\sim 5$ cm^2/s were observed for both the icosahedral and crystalline phases. These values, while larger than those found in previous i-phase samples, still suggest considerable disorder within these samples to account for the observed electronic diffusivity.[21] However, in stable i-$Al_{56.1}Cu_{10.2}Li_{33.7}$ (Ref. 9), where the DOS was found to be 30% of its free-electron value, a value of $\rho = 95$ $\mu\Omega$ cm then yields $D\sim 11$ cm^2/s. This D value is substantially larger than those observed in previous alloys. Values of D obtained from experimentally measured DOS and ρ values for samples in this study and from previous work (Ref. 9) are listed in Table I. As can be seen, $D\sim 2.5$ cm^2/s for i-$Al_{75}Cu_{20}V_{10}$ is comparable to that found in the initial i-phase samples with small mean free paths, while that of i-$Ga_{16}Mg_{32}Zn_{52}$, $D\sim 20$ cm^2/s, is even larger than that obtained for i-$Al_{56.1}Cu_{10.2}Li_{33.7}$. Thus, the electronic diffusivities of these stable i phases are an order of magnitude greater than those first reported. Our results provide evidence that the transport properties of some i-phase samples are distinctly different from those of glassy alloys, but similar to those of crystalline compounds.

In conclusion, we have shown that the stable i phases of Ga-Mg-Zn, Al-Cu-Li, and Al-Cu-Fe are all characterized by significantly lower values in the electronic DOS as compared to their free-electron values, which may be a key to their unusual stability. This suggests that these icosahedral alloys may qualitatively be described as Hume-Rothery phases. i-$Al_{75}Cu_{15}V_{10}$ is found to have a DOS quite close to its free-electron value, which has also been observed in other metastable quasicrystals [Al-Mg-Zn (Ref. 8) and Al-Cu-Mg (Refs. 9 and 21)]. i-$Al_{65}Cu_{20}Fe_{15}$, prepared both by rapid quenching and from an anneal of bulk samples, is found to exhibit spin-glass-like behavior at low temperature, confirmed both by specific-heat and ac susceptibility measurements. However both samples show markedly different magnetic behavior at low temperature, with the melt-spun i phase being more magnetic. The differences in magnetic and vibrational properties are likely linked to structural differences. For i-$Ga_{16}Mg_{32}Zn_{52}$, an electronic diffusivity of ~ 20 cm^2/s is observed, which is the largest reported value to date for icosahedral alloys. The large electronic mean free paths found in the stable i phases of Ga-Mg-Zn and Al-Cu-Li (Ref. 9) as compared with previous quasicrystalline compounds suggest a better ordered icosahedral material.

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