Band-Structure Effects on the Electronic Properties of Icosahedral Alloys

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Distinct deviations from smooth trends of the Hall coefficient, thermopower, and electronic specific heat with the composition in icosahedral AlCuMg and GaZnMg alloys are observed. These arise in regions where the free-electron Fermi wave vector is predicted to lie near Bragg planes determined from strong x-ray-diffraction maxima. Our results provide the first experimental evidence for anomalies in the electronic density of states near the Fermi level in these alloys, which may be important in the stabilization of this class of icosahedral phases via Hume-Rothery considerations.

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The consequence of icosahedral (i) symmetry on the electronic properties of the i phase[1,2] and possible electronic mechanisms for the formation and stability of these materials has received much theoretical attention.[3,4] Perhaps the most striking of proposed properties is the presence of strong Van Hove singularities in the densities of states (DOS) associated with the large multiplicity of strong peaks in the structure factor. Theoretical calculations based on i-Al with a single atom per three-dimensional Penrose tiling[2,3] have indeed predicted sharp features in the DOS which may be observable by various experimental techniques. However, direct experimental evidence of such effects has not been reported. Attempts to directly observe the profile of DOS by use of soft-x-ray emission measurements[5] can only place limits on the magnitude and scale of these anomalies due to inherent broadening effects which limit the energy resolution to $\sim$0.25 eV. Thermodynamic and transport measurements as functions of temperature and alloy composition can sample a much narrower energy region of less than 0.01 eV. Such measurements are therefore expected to be a very sensitive probe of electronic structures near the Fermi level.

In this paper, we present the results of a systematic study of the Hall coefficient, thermopower, and specific heat of i-$Al_{100-x-y}Cu_xMg_y$ ($x=4$–19, $y=35$–39) and i-$Ga_{100-x-y}Zn_xMg_y$ ($x=37$–46, $y=33$–37). These systems were chosen for a detailed study of electronic and transport properties since (1) they contain only simple and noble metals which permits a straightforward calculation of the free-electron parameters, and (2) single-phase samples can be obtained over a relatively large composition range[6] thus providing means to investigate the role of these parameters on electronic properties. In addition, the i phases of AlCuMg and GaZnMg are expected to be structurally similar, and their ranges of i-phase formation span different values of nearly-free-electron (NFE) parameters with a small overlap.

All samples used in this study were prepared by melt spinning in an argon atmosphere with wheel speeds of 3000 to 5500 rpm yielding thin ribbons $\sim$15–30 μm thick and 1–2 mm wide. The structure of the i phase was confirmed by x-ray diffraction which also provided information on the quasilattice constant a_r and the relative amount of disorder present. The Hall coefficient and resistivity were measured simultaneously between 4.2 and 300 K on a given sample by means of six leads in the appropriate configuration attached to the sample by silver paint.[7] The Hall voltage was measured in a 4-T field using a Keithley 181 nanovoltmeter with a typical current density of 20–40 A/cm^2. Thermoelectric power was measured by the differential method with respect to high-purity lead wires in the temperature range of 4.2–300 K. Specific-heat measurements were performed in a previously described relaxation calorimeter[8] in the temperature range 0.7–7 K. Samples used for specific-heat measurements were pressed pellets for all AlCuMg and most of the GaZnMg samples for which x-ray diffraction showed no indication of transformation resulting from the pressing process.

In calculating the free-electron parameters of the i phases of AlCuMg and GaZnMg, the average valence Z is obtained by assuming an effective valence of three for Al and Ga, two for Mg and Zn, and one for Cu. The magnitude of the NFE Fermi wave vector is then given by $k_F=(3\pi Z/V)^{1/3}$, where V is the average atomic volume. Over 25 individual, single-phased samples of i-$Al_{100-x-y}Cu_xMg_y$ ($x=4$–19, $y=35$–39) were prepared which span a range of values $Z=2.24$–2.54 e/atom, $k_F=1.539$–1.584 Å^{-1}, and $a_r=5.104$–5.210 Å as determined by x-ray diffraction. It is important to note that a systematic variation in a_r was observed throughout the range of formation indicating a true compositional variation of the i phase. For i-$Ga_{100-x-y}Zn_xMg_y$ ($x=37$–46, $y=33$–37), which forms over a more limited compositional range than i-AlCuMg, eight samples were prepared with corresponding values of $Z=2.18$–2.28 e/atom, $k_F=1.507$–1.520 Å^{-1}, and $a_r=5.097$–5.124 Å. Formation of the i phase in these two systems is found to occur in regions where $2\mathbf{k}_F$ is nearly degenerate with the reciprocal-lattice vectors related to the (222100) and (311111)/(222110) x-ray-diffraction peaks (using the index notation of Ref. 9) for i-GaZnMg and i-AlCuMg, respectively. As first sug-

gested in Ref. 10, the icosahedral structure may be stabilized through energetic considerations when the Fermi surface intersects Jones zone boundaries via standard Hume-Rothery arguments. Rephrasing the latter condition in terms of the valence Z, the i phases are then expected to form near certain electron-per-atom ratios, Z_c's, of 2.17 and 2.42 e/atom (Ref. 2). The Z_c's are calculated using the structural model of Ref. 11 and estimating the average atomic density as that of the related Frank-Kasper phase. However, in real alloys, slight deviations from these Z_c values obtained from the NFE model are expected. It is important to stress that for each alloy system, the experimental properties measured are found to be quite insensitive to the particular composition; rather, they are only dependent on the average valence Z value.

Resistivities of single i-phase samples in these systems are observed to be essentially temperature independent (changing less than $\pm 5\%$ for AlCuMg and $+15\%$ for GaZnMg samples between 4.2 and 300 K, with room temperature values of ~ 50–$180\ \mu\Omega\,\mathrm{cm}$). Similarly, the measured Hall coefficients were also found to be temperature independent. Values of R_H are reported at 300 K. The largest contribution to the uncertainties in the Hall measurements arise from irregularities in sample geometry. For i-AlCuMg samples, the ribbons are found to be very uniform and the reproducibility of R_H is typically better than 10%. The reproducibility of the i-GaZnMg samples, on the other hand, is closer to 20%, reflecting the less uniform nature of these samples observed. Values of R_H shown for i-GaZnMg are obtained by averaging values measured for several samples. Plots of R_H vs Z are shown in Figs. 1(a) and 1(b). There are distinct regions, near $Z \sim 2.24$ e/atom for i-GaZnMg, and $Z \sim 2.26, 2.40$ e/atom for i-AlCuMg, where abrupt changes exist in the trends of R_H. Similar behavior is also seen in trends of the thermopower and specific heat. It is precisely in these regions where the NFE values of k_F are found to intersect zone planes as observed by x-ray diffraction. It is interesting to point out that the largest deviation for the i-AlCuMg data occurs near $Z \sim 2.26$ and is quite similar in shape and magnitude to that observed in the i-GaZnMg data at nearly the same Z value. The magnitudes of R_H greatly exceed their NFE values over most of the i-phase formation range, suggesting the effective carrier densities in these regions are significantly reduced. The NFE values of R_H are ~ -0.60 and -0.54×10^{-24} cgs units for i-GaZnMg and i-AlCuMg, respectively. In the i-AlCuMg samples, the trend in R_H begins to approach the predicted NFE values at the highest Z values.

Room-temperature thermopower measurements are shown in Figs. 2(a) and 2(b). The reproducibility of these measurements is typically better than 1% (on the order of the symbol size). The thermopower data exhibit positive curvatures in the temperature dependence, a signature of electron-phonon interaction.[12] No evidence of phonon-drag effects are observed. The magnitude of the thermopower, which depends on the energy derivative of the resistivity, can be estimated from trends in the compositional dependence of the measured resistivity[7] and NFE values of E_F by the Mott formula.[12] The range of values (-4 to -8 μV/K) calculated accounts well for the trend of the thermopower data observed in these alloys. Again, there exists clear structure in regions consistent with that observed in the Hall data. Based on

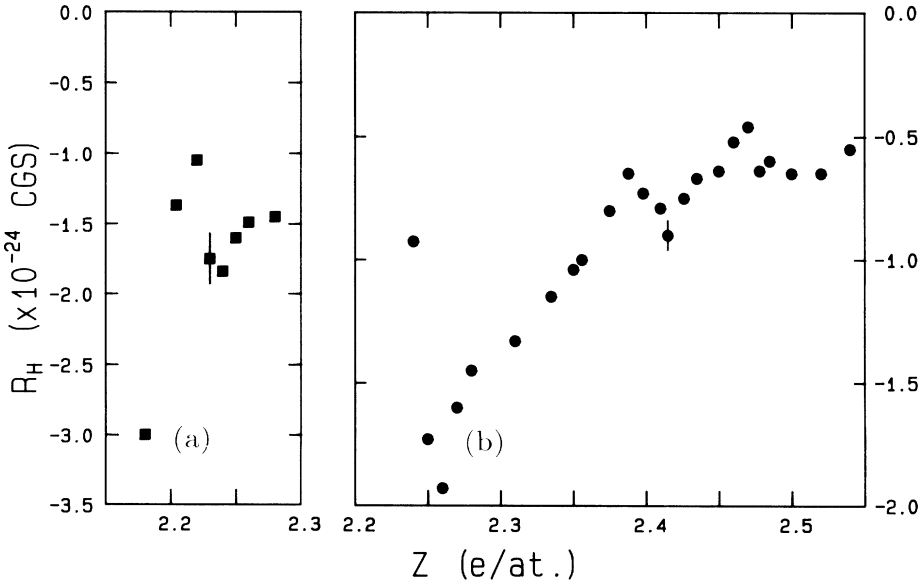

FIG. 1. Room-temperature values of the Hall coefficient vs Z of (a) i-GaZnMg and (b) i-AlCuMg samples. Representative uncertainties in the measurements are shown for each system.

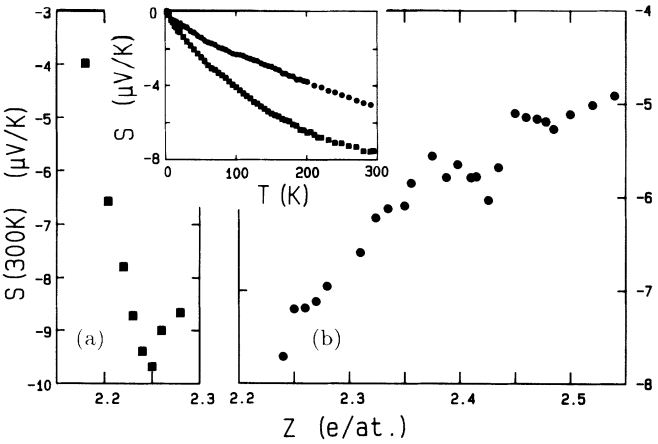

FIG. 2. Room-temperature values of the thermopower vs Z of (a) i-GaZnMg and (b) i-AlCuMg samples. Typical temperature dependences of the thermopower for (■) i-GaZnMg and (●) i-AlCuMg are shown in the inset.

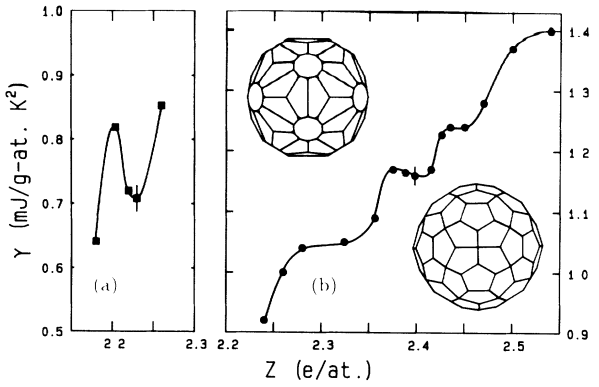

FIG. 3. Low-temperature values of the electronic coefficient of specific heat of (a) i-GaZnMg and (b) i-AlCuMg; solid lines are guides for the eye. Also, the pseudo Jones zones 1 and 2, as discussed in the text, are shown in the upper left-hand side and lower right-hand side of (b).

NFE estimates, these structures are observed within an energy range of ~0.2 eV, which is beyond the resolution of soft-x-ray emission measurements.[5]

In Figs. 3(a) and 3(b), the electronic coefficients of specific heat for i-GaZnMg and i-AlCuMg are shown. The linear electronic coefficient (γ) and the lattice contributions were separated from the total specific heat by fitting the data with the standard $C=\gamma T+\beta T^3+\delta T^5$ expression.[13] Similar weights of samples were measured by identical technique over the same temperature range and analyzed in a consistent manner, thus providing confidence in the results observed. For i-GaZnMg samples, the presence of significant T^5 terms even at the lowest temperature (~0.7 K) measured, combined with small values of γ, introduces a somewhat larger uncertainty in the determination of γ (~8%) than for i-AlCuMg (~3%). The γ values of i-GaZnMg exhibit a rather rapid variation on the mean valence Z, with a minimum near Z of 2.23 e/atom and a significant increase (up to 15%) as Z is varied from this value. For i-AlCuMg, an overall smoother variation of γ with Z is observed; however, distinct deviations occurring near Z of 2.25 and 2.4 e/atom are noted.

By comparing experimental values of reciprocal-lattice vectors with $2k_F$ values, the free-electron Fermi sphere is found to make contact with zone planes corresponding to the (222100) and (311111)/(222110) reciprocal-lattice vectors near $Z\sim2.2$ and 2.4 e/atom, respectively. Construction of these pseudo Jones zones,[14] assuming perfect icosahedral symmetry, is straightforward. The zones resulting from this construction are shown in Fig. 3(b). Zone 1 (upper left-hand side) and zone 2 (lower right-hand side) consist of 132 and 72 planes, respectively, and are seen to be nearly spherical due to the large multiplicity of the vectors. The effects due to deviations from ideal icosahedral symmetry, present in these alloys, would be the distortion of these zones.

The most direct information about the DOS at the Fermi level is from the electronic specific-heat coefficient $\gamma=\frac{2}{3}\pi^2k^2N(\epsilon_F)(1+\lambda)$, where λ is the electron-phonon coupling constant. Values of λ can be calculated from experimental values of Θ_D from specific heat and T_c for superconducting samples.[8] For these low-T_c (<1 K) samples, λ values are small (~0.4) and show only a modest variation over the range of i-phase formation. Therefore, it is reasonable to expect that the compositional dependence of γ directly reflects the dependence of the DOS. For i-AlCuMg the DOS varies from ~75% to ~105% of its NFE value at $Z=2.25$, 2.54 e/atom, respectively, while that of i-GaZnMg changes from ~54% to ~66% of its NFE value as the electron concentration increases from 2.18 to 2.26 e/atom. Consistent with the concentrations of effective carriers deduced from the Hall measurements, the DOS's from the specific-heat results are significantly reduced below NFE values at low Z with the DOS's regaining NFE values at the highest Z values. This behavior can be accounted for by the reduction of Fermi surface area due to interaction with the set of gaps associated with the zone planes shown in the insets of Fig. 3(b). Contact of the Fermi sphere with the first and second set of zone planes occurs near ~2.2 and ~2.4 e/atom, respectively, with the Fermi surface clearing both zones when Z exceeds ~2.7 e/atom. Thus, one would expect deviations from NFE behavior over most of this range except near the highest Z values, as observed. It is also important to stress that the magnitude of these gaps is affected by both the multiplicity of planes near the Fermi surface and the effective pseudopotential of the metal. Since the strength of the pseudopotential of Cu is substantially larger than that of Al (Ref. 15), it is likely that the effects of these pseudogaps in i-AlCuMg are largest at lower Z values (where the alloys are more Cu rich). Additionally, the pseudogaps are expected to be large for the i phases of GaZnMg since both Ga and

Zn have large pseudopotentials. Based on this, one would expect the observed deviations to be most pronounced for the *i* phases of GaZnMg and those of AlCuMg with small Z values. This is in accordance with that seen in the experimental data, especially the behavior of R_H and γ.

Disorder present in these alloys would tend to smooth out the features due to these singularities in the DOS. Values of peak widths from x-ray diffraction of *i*-GaZnMg are up to 20% narrower than those of *i*-AlCuMg, suggesting that the *i* phases of GaZnMg data tend to be sharper and more pronounced than those of the AlCuMg data. Linear phason strain, a special disorder related to the incommensurate nature of quasicrystals, has been proposed to account for the asymmetries and broadening of diffraction peaks of these icosahedral alloys.[16] The effect of such a strain would be to shift the otherwise degenerate reciprocal-lattice vectors away from their ideal icosahedral values. If present, this would give rise to additional features near regions where the Fermi sphere is expected to intersect zone planes associated with these vectors. Strong evidence of this behavior exists most noticeably in the Hall and thermopower data (and to a lesser extent in the specific-heat data) in the region of $Z=2.4$–2.5 e/atom, where two breaks in the trends of the data exist. It would therefore be interesting to attempt to study icosahedral alloys which are free from these defects, as in the new class of stable *i* phases of AlCuFe and AlCuRu.

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