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Soft-x-ray, heat-capacity, and transport measurements on icosahedral and crystalline alloys

P. A. Bruhwiler, J. L. Wagner, B. D. Biggs, Y. Shen, K. M. Wong, S. E. Schnatterly, and S. J. Poon
Jesse Beams Laboratory of Physics, University of Virginia, Charlottesville, Virginia 22903

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Soft-x-ray emission, heat-capacity, and resistivity measurements are reported for icosahedral and Frank-Kasper phases of Al-Cu-Li and Al-Cu-Mg. This is the first extensive comparison of electronic properties of periodic and quasiperiodic lattices generated by packing similar structural units. Results are compared with theories of quasicrystals and provide a guideline for the observability of Van Hove singularities in quasicrystals. The density of states $N(0)$ is a factor of 3 less in Al-Cu-Li than in Al-Cu-Mg alloys; this is spectroscopically confirmed.

Since the discovery of the first quasicrystalline Al-Mn phase[1] which exhibits an icosahedral point symmetry incompatible with translational periodicty, much experimental work has been focused on their structures,[2] but comparatively little has been done on electronic properties. Theoretical studies of the effect of quasiperiodicity on electronic structure[3-5] and transport[6] for Penrose lattices have been undertaken. Calculations[6] indicate that quasiperiodicity alone could not account for the high resistivity observed in some of the first icosahedral alloys,[7,8] which was considered to be caused by structural defects and *s-d* interactions. These high-resistivity values tend to suggest that the transport properties of icosahedral alloys are similar to those of metallic glasses. The need to clarify this point is one reason that recently more attention is being given to simple metal alloys.[8,9] Combining soft-x-ray emission studies, which provide information on the density of occupied states and other electronic measurements such as heat capacity and conductivity, can result in a more complete understanding of electronic properties of icosahedral and corresponding crystalline materials, allowing comparison with theoretical predictions. So far, experimental density-of-states (DOS) studies have been limited by compositional differences between the crystalline and icosahedral phases chosen.[10,11]

In this article, we present results from soft-x-ray emission (SXE), heat capacity, and electron transport studies of Al-Cu-(Mg,Li) icosahedral (*I*) and Frank-Kasper (FK) phases. We chose these because high-quality single-phase samples can be obtained,[12] and the two phases have the same composition and similar structural units[12-14] in each case. Thus, comparison of properties of periodic and quasiperiodic lattices resulting from packing similar structural units can be made. Moreover, the effect of *d* states on the Fermi-level DOS should be minimal in these systems, enabling comparison with a free-electron (FE) model. Measurements of transport and heat capacity reflect the Fermi-level DOS nature. On the other hand, SXE studies provide information on deeper states since in SXE spectra the intensity profile provides a measure of the DOS local to the emitting atoms, modified by a transition probability which for simple FE-like metals varies little over the bandwidth of the electron states. Thus, SXE complements the techniques noted above, and enables us to unveil electronic properties of these quasicrystalline alloys through combined studies. We have also modeled the SXE data in a manner which for the first time allows direct comparison to the heat-capacity results.

Sample preparation has been described in detail elsewhere.[12] The samples were in the form of melt-spun ribbons for *I*-$Al_{56}Cu_{10}Li_{34}$, *I*-$Al_{51}Cu_{12.5}Mg_{36.5}$, and FK-$Al_{51}Cu_{12.5}Mg_{36.5}$ (annealed); and as-cast ingots for FK-$Al_{56}Cu_{10}Li_{34}$. Our SXE spectrometer[15] and data processing[10] have been described previously. The samples were excited by a 3 kV electron beam (size $=0.1\times1$ mm^2, 0.3 mA), and we have corrected the data for spectrometer response. Each spectrum represents a transition DOS with a background[16] which is of no consequence when comparing spectra. Heat-capacity measurements were performed using the thermal relaxation method at temperatures ranging from 0.8 to 10 K. Resistivity measurements (0.4 to 300 K) were carried out by the four-terminal method. A more detailed discussion of these procedures will be given elsewhere.[17]

We have measured Al and Mg $L_{2,3}$ emission and Li K emission spectra of the pure metals and in the alloys. Pure Al $L_{2,3}$ emission is fairly well described by a FE picture, with a DOS varying as $(E-E_0)^{1/2}$, a sharp cutoff in the DOS at threshold $(=E_0+E_F)$, and a bandwidth of 10.7 eV[16], which is 0.9 eV less than the FE value. This simple scheme must be modified by including effects of the band structure,[5,18] and other influences.[16,18,19] However, SXE has been used successfully to compare alloy systems[10,20,21] without explicitly considering all such effects.

Al $L_{2,3}$ emission data from the alloys and the pure metal are presented in Fig. 1. The alloy spectra clearly differ from each other and pure Al, but there are features common to all the spectra. More importantly, spectra from *I* and FK phases of the same composition resemble each other. The common features are the position of the threshold (72.7 eV) and the bandwidth (or E_F), which is within a few tenths of an eV of the pure Al value. The Al-Cu-Mg spectra of both phases possess a threshold singularity like those of simple metals,[18] while the Al-Cu-Li systems display instead a rounded peak just below threshold.

Mg $L_{2,3}$ emission spectra from the Al-Cu-Mg *I* and FK phases are shown in Fig. 2. The overall shape for each al-

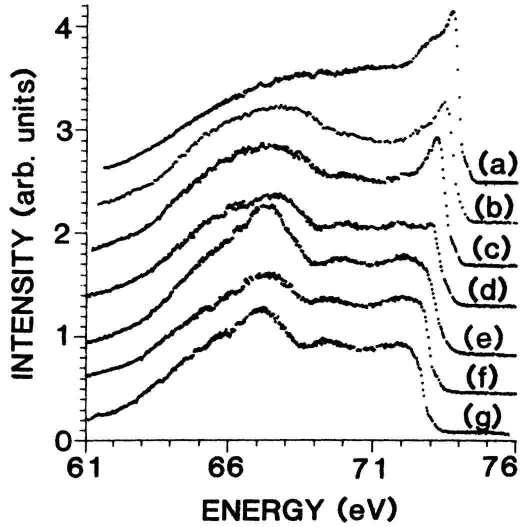

FIG. 1. Al $L_{2,3}$ emissions spectra of (a) pure Al, (b) FK- and (c) I-$Al_{51}Cu_{12.5}Mg_{36.5}$, (d) I-$Al_{51}Cu_{12.5}Mg_{20}Li_{16.5}$, (e) I-$Al_{51}Cu_{12.5}Mg_{10.6}Li_{20.9}$, (f) I- and (g) FK-$Al_{56}Cu_{10}Li_{34}$. Each spectrum is shifted up in energy by 0.2 eV relative to the one below.

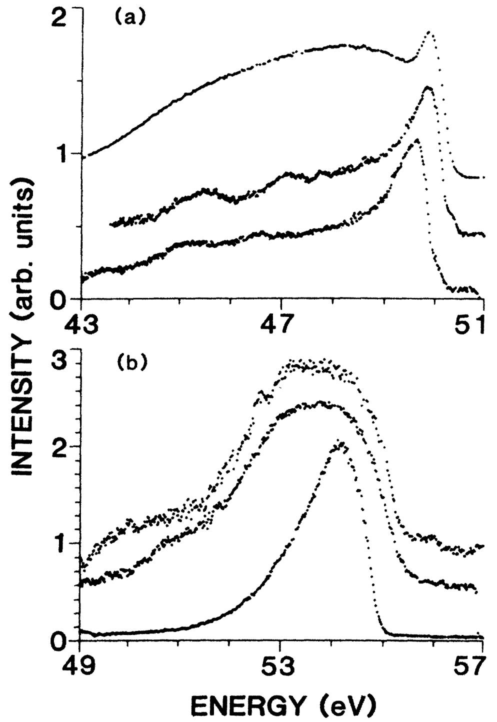

FIG. 2. (a) Mg $L_{2,3}$ emission spectra of, from top to bottom, pure Mg, I- and FK-$Al_{51}Cu_{12.5}Mg_{36.5}$. The pure Mg and I-phase spectra are shifted up by 0.6 eV and 0.3 eV, respectively. (b) Li K emission spectra of, from top to bottom, FK- and I-$Al_{56}Cu_{10}Li_{34}$, and pure Li.

loy is reminiscent of earlier results on Al-Mg alloys,[20] with the peaking at threshold (49.84 eV) dominating the spectrum. The bandwidth appears to be ~1 eV less than that of Mg metal, but the s,d-like DOS may simply be damped by lifetime effects.[16,19] Also presented in Fig. 2 are the Li K emission spectra of the Al-Cu-Li systems, which continue the trend of similarity between the I and FK phases. The data are not as sharply peaked as the pure Li spectrum, and to our knowledge such a wide, evenly distributed DOS has not been seen before in Li; earlier experimental work on Li alloys includes SXE studies of Li-Mg and Li-Al.[22]

The heat-capacity measurements are summarized in Fig. 3 (only Al-Cu-Li data are shown, without including data on the superconducting transitions) and Table I. The coefficient of the electronic contribution to the heat capacity (γ) is determined from the intercept of this plot, and the Debye temperature Θ_D, from the slope of the line. The I and FK phases are superconductors, with transition temperatures T_c (determined both from resistivity and heat-capacity measurements) listed in Table I. Resistivities (ρ) of Al-Cu-Mg and Al-Cu-Li alloys are reported for melt-spun and as-cast samples, respectively. The electron-phonon coupling constant λ is found from T_c and Θ_D using the McMillan T_c equation ($\mu^* = 0.13$). We obtain the DOS at the Fermi level [$N(0)$] knowing λ and γ. Also listed is the FE DOS $N_f(0)$. It is noted that $N(0)$ for both Al-Cu-Mg systems is close to the FE value, but for the Al-Cu-Li alloys is a factor of 3 less.

Resistivity values for I-Al-Cu-Mg and Al-Zn-Mg (Ref. 9) are quite comparable to their corresponding FK-phase values. Electronic mean free paths (l) estimated using the FE model for these systems range from 7 to 10 Å. On the other hand, I-Al-Cu-Li appears to have significantly larger ρ than FK-Al-Cu-Li. Taking the $N(0)$ factor into account when estimating l for I-Al-Cu-Li, however, yields a value of ~20 Å. This value is much larger than those (1–10 Å) encountered in metallic glasses and highly disordered systems. Thus, our results show that the transport properties of icosahedral crystals are similar to those of crystalline alloys.

To quantify the broadening effects in the emission data, we modeled the threshold shape with a modified step function which included Gaussian broadening.[10] This model

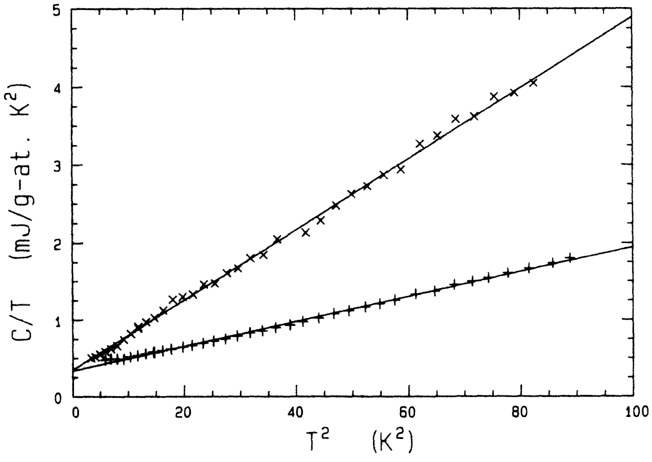

FIG. 3. Heat-capacity results for (upper curve) I- and (lower curve) FK-$Al_{56}Cu_{10}Li_{34}$.

TABLE I. Heat-capacity and transport results.

	ρ (4.2 K) ($\mu\Omega$ cm)	T_c (K)	γ (mJ/g-at. K^2)	Θ_D (K)	λ	$N(0)$ (states/eV atom)	$N_f(0)$ (states/eV atom)
			$Al_{56}Cu_{10}Li_{34}$				
FK	38	< 0.40	0.34 ± 0.03	494	· · ·	· · ·	0.34
I	93	1.48	0.35 ± 0.04	350	0.47	0.10	
			$Al_{52.4}Cu_{12.6}Mg_{35}$				
FK	52	0.73	1.12 ± 0.09	342	0.40	0.34	0.38
I	65	0.81	1.09 ± 0.11	295	0.42	0.33	

for the edge should be adequate for comparison if confined to energies above the halfway point of the edge. The half-width (Γ) of the Gaussian and the edge position further characterize the data. The results of these fits are summarized in Table II. We find a pure Al threshold energy of 72.69 eV in agreement with earlier work[23] which we find for all of the Al emission presented here. The values of Γ obtained for each alloy component are $\frac{1}{3}$ higher ($\frac{1}{2}$ higher) than those found for the pure metal *L* (*K*) emission data. This is expected due to the multiple possibilities of electronic environment for each metal in the alloys,[12,13] and has been discussed previously.[10] All the Al spectra yield essentially the same value of Γ, as do both Mg spectra; the Li spectra give differing values.

At first glance the correlation between the Al *L* emission data and the DOS results of heat-capacity measurements seems apparent—the amplitude of the Al-Cu-Mg edge is about 1.5 times that of the Al-Cu-Li edge, once the spectra are normalized to the same height at lower energies. Most of this amplitude difference, however, is due to the Mahan-Nozières-De Dominicis (MND) singularity, a many-body effect. A theoretical review of the MND model is given in Ref. 24. The form of this peaking is a power law $(E_F - E)^{-\alpha}$ near threshold, by which any model DOS must be multiplied before it is broadened to fit data. Two possibilities suggest themselves: (1) the excitonic MND enhancement is somehow disallowed by the presence of Li, or (2) the DOS near threshold is much lower in the Li-containing alloy, so that the resultant spectrum has a "hidden" enhancement. Since the DOS at E_F is much lower in Al-Cu-Li than Al-Cu-Mg, and x-ray experiments have indicated that α does not vary significantly on going from a pure metal to an alloy,[25] the second choice is more likely. We modeled the *I* phase with a more sophisticated function to test this idea. The usual model for x-ray edge data is a step function to represent the DOS, multiplied by the MND power law and broadened by a Lorentzian (to represent the effect of the finite core lifetime) and a Gaussian (for phonon, temperature, and instrumental effects). We chose to include the more general possibility of a sloped DOS just below E_F. We have modeled the emission edges of *I* phase Al-Cu-Mg and Al-Cu-Li with the following convolution function:

$$F(E) = Af(E_t - E) + Bf(E_t + \Delta - E) \ ,$$

where

$$\begin{aligned} f(E) = \int_{-\infty}^{\infty} dE''(2\pi\sigma^2)^{-1/2} \exp[-\tfrac{1}{2}(E-E'')^2/\sigma^2] \\ \times \int_{-\infty}^{\infty} dE' \pi^{-1} \frac{\gamma/2}{(E''-E')^2 + (\gamma/2)^2} \Theta(-E') \\ \times |E'|^{-\alpha}(1+mE') \ . \end{aligned}$$

The parameters are defined as follows: E_t is the threshold energy, Δ is the spin-orbit splitting of the core, Θ is the Heaviside step function, α is the MND exponent, m is the DOS slope, Γ is the Lorentzian half-width, and 2.354σ is the Gaussian half-width. This is generally accepted as accounting for all effects on the edge shape except self-absorption. We seek amplitudes *A* and *B* in the model, which summed give the strength contributed by the DOS at E_F, (i.e., E_t) to the edge intensity. This fact makes self-absorption effects negligible since the L_3 edge shape,

TABLE II. Threshold energy (E_t) and half-width (Γ) (measured in eV) obtained from fits to the emission spectra at the conduction edges, using a modified step function model.

	Al		Mg		Li	
	E_t	Γ	E_t	Γ	E_t	Γ
			$Al_{56}Cu_{10}Li_{34}$			
I	72.68 ± 0.04	0.29 ± 0.02	· · ·	· · ·	54.96 ± 0.05	0.70 ± 0.05
FK	72.69 ± 0.04	0.36 ± 0.03	· · ·	· · ·	55.05 ± 0.05	0.54 ± 0.05
			$Al_{51}Cu_{12.5}Mg_{36.5}$			
I	72.69 ± 0.04	0.27 ± 0.02	49.83 ± 0.03	0.16 ± 0.02	· · ·	· · ·
FK	72.70 ± 0.01	0.28 ± 0.01	49.85 ± 0.03	0.17 ± 0.03	· · ·	· · ·
			Pure element			
	72.68 ± 0.01	0.21 ± 0.01	49.57 ± 0.01	0.13 ± 0.01	54.67 ± 0.01	0.43 ± 0.01

which is almost unaffected by self-absorption, is by far the major factor in determining α and m, and contributes over 80% of the intensity at threshold. α is chosen to be a typical value for Al (see Ref. 18 for a summary), about 0.16. We obtained $(A+B)_{\text{Al-Cu-Mg}}=1.10$ and $(A+B)_{\text{Al-Cu-Li}}=0.60$ after normalizing the spectra at 70 eV; m for these fits is about 0.1 and -0.7, respectively. We checked other values and found (for low chi-squared) that the ratio of summed amplitudes varied by less than 5% over a wide range of α's. The SXE-derived $N(0)$ ratio is thus 1.8, significantly less than the 3.4 given by heat-capacity results. However, the spectral broadening in our SXE data (see Table II) is ~ 250 meV compared to 0.5 meV for the thermodynamic experiment, so that $N(0)$ obtained in this new way is an average over many more states than in the thermodynamic experiment, and the agreement between the two ratios is reasonable.

The most recent calculation of a 3D quasicrystal DOS (Ref. 5) indicates large Van Hove singularities might be observable in the DOS due to certain peaks in the structure factor. The intrinsic limit of resolution of DOS features by any valence-band spectroscopy is given by the lifetime broadening of the valence hole left behind in all such measurements (e.g., SXE or photoemission). This Lorentzian broadening has a width which varies approximately quadratically with energy below E_F.[16,19] In the present case, all other sources of broadening have a combined width of about 0.25 eV. Thus any structure like the large peaks shown for quasicrystal Al in Ref. 5 would be easily resolved if it lay within 4 eV of E_F, since the total broadening function is conservatively 0.6 eV wide at that energy in Al.

In real systems studied so far the structure factors of crystal and quasicrystal phases of the same composition are quite similar[12] over the range of Q values (1–3.5 Å^{-1}) which could produce structure in our data within ~ 8 eV of E_F. This is in contrast to the quasicrystal Al to fcc Al comparison cited above for which the structure factors are quite different. Thus Marcus's result[4] is consistent with our measurements in not predicting striking changes in the electronic DOS between alloys with similar structure factors. The feature at ~ 69.5 eV in the Al spectra could be due partly to Van Hove singularities, but probably receives most of its strength from Cu d states;[26] the same is true for the small peak in the alloy Mg spectra which appears 3 eV below E_F.[27] The bump at ~ 45 eV in the Mg spectra arises in Al-Mg alloys as well.[22] In conclusion, density-of-states differences between crystalline and quasicrystalline phases of the same alloy will be observable only when the structure factors differ significantly.

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[1] D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984).

[2] For a review, see *Conference Proceedings of the International Workshop on Aperiodic Crystals* [J. Phys. (Paris) Colloq. **47**, C3 (1986)]; C. L. Henley, Comments Condens. Matter Phys. **13**, 59 (1987).

[3] M. E. McHenry, M. E. Eberhart, R. C. O'Handley, and K. H. Johnson, Phys. Rev. Lett. **56**, 81 (1986). For 2D cases, see e.g., H. Tsunetsugu, T. Fujiwara, K. Veda, and T. Tokihiro, J. Phys. Soc. Jpn. **55**, 1420 (1986); M. Kohmoto and B. Sutherland, Phys. Rev. Lett. **56**, 2740 (1986), and references therein.

[4] M. A. Marcus, Phys. Rev. B **34**, 5981 (1986).

[5] A. P. Smith and N. W. Ashcroft, Phys. Rev. Lett. **59**, 1365 (1987).

[6] J. B. Sokoloff, Phys. Rev. Lett. **57**, 2223 (1986); Phys. Rev. B **36**, 6361 (1987).

[7] See, e.g., K. M. Wong and S. J. Poon, Phys. Rev. B **34**, 7371 (1986); D. V. Baxter, R. Richter, and J. O. Strom-Olsen, *ibid.* **35**, 4819 (1987); P. Pavuna, C. Berger, F. Cyrot-Lackman, P. Germi, and A. Pasturel, Solid State Commun. **59**, 11 (1986); M. J. Burns, A. Behrooz, X. Yan, P. M. Chaikin, P. Bancel, and P. Heiney, Bull. Am. Phys. Soc. **31**, 268 (1986).

[8] K. M. Wong, E. Lopdrup, J. L. Wagner, Y. Shen, and S. J. Poon, Phys. Rev. B **35**, 2494 (1987).

[9] J. E. Graebner and H. S. Chen, Phys. Rev. Lett. **58**, 1945 (1987).

[10] P. A. Bruhwiler, Y. Shen, S. E. Schnatterly, and S. J. Poon, Phys. Rev. B **36**, 7347 (1987).

[11] K. L. Tsang *et al.*, Bull. Am. Phys. Soc. **32**, 686 (1987).

[12] Y. Shen, S. J. Poon, W. Dmowski, T. Egami, and G. J. Shiflet, Phys. Rev. Lett. **58**, 1440 (1987); W. Dmowski, T. Egami, Y. Shen, S. J. Poon, and G. J. Shiflet, Philos. Mag. Lett. **56**, 63 (1987).

[13] C. L. Henley and V. Elser, Philos. Mag. B **53**, L59 (1986).

[14] Y. Ma, E. A. Stern, and F. W. Gayle, Phys. Rev. Lett. **58**, 1956 (1987).

[15] R. D. Carson *et al.*, Rev. Sci. Instrum. **55**, 1973 (1984).

[16] P. Livins and S. E. Schnatterly, Phys. Rev. B (to be published).

[17] J. L. Wagner, B. D. Biggs, K. M. Wong, Y. Shen, and S. J. Poon (unpublished).

[18] P. H. Citrin, G. K. Wertheim, and M. Schlüter, Phys. Rev. B **20**, 3067 (1979).

[19] See, e.g., E. W. Plummer, Surf. Sci. **152–153**, 162 (1985).

[20] H. Neddermeyer, in *Band Structure Spectroscopy of Metals and Alloys*, edited by D. J. Fabian and L. M. Watson (Academic, New York, 1973), p. 153.

[21] A. Mansour, S. E. Schnatterly, and J. J. Ritsko, Phys. Rev. Lett. **58**, 614 (1987).

[22] J. A. Tagle, E. T. Arakawa, and T. A. Callcott, Phys. Rev. B **22**, 2716 (1980); R. S. Crisp, J. Phys. F **11**, L219 (1981); **13**, 1317 (1983).

[23] C. Park and T. Sagawa, J. Appl. Phys. **60**, 1310 (1986).

[24] U. von Barth and G. Grossman, Phys. Rev. B **25**, 5150 (1982).

[25] S. Suzuki *et al.*, Solid State Commun. **50**, 769 (1984).

[26] D. J. Fabian, G. McD. Lindsay, and L. M. Watson, in *Electronic Density of States*, edited by L. H. Bennett, Natl. Bur. Stand. Special Publ. 323 (NBS, Washington, DC, 1969), p. 307; J. C. Fuggle, E. Källne, L. M. Watson, and D. J. Fabian, Phys. Rev. B **16**, 750 (1977).

[27] H. Neddermeyer, Phys. Status Solidi B **78**, 609 (1976).