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A resonant photoemission study of the $Al_{65}Cu_{20}Ru_{15}$ icosahedral alloy

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Abstract. Measurements with photoemission spectroscopy in the photon-energy range 41–140 eV have been used to determine the valence band of the stable icosahedral $Al_{65}Cu_{20}Ru_{15}$. An investigation of resonant photoemission near the Ru 4p→4d transition shows that the feature in the valence band with the maximum intensity at 1.3 eV below the Fermi level is predominantly due to the Ru 4d-derived states. This has been additionally confirmed by measuring the photoemission spectra in the constant-initial-state mode and by employing the effect of the Cooper minimum in the photoionization cross section of the Ru 4d orbitals. The feature in the valence band with the maximum intensity at 3.8 eV below the Fermi level has been identified as being due predominantly to the Cu 3d-derived states. The strong decrease of intensity towards the Fermi level has been interpreted as being indicative of the presence of a pseudo-gap at the Fermi level. It has been indicated, however, that the Fermi cut-off also contributes to the observed intensity decrease. No unusual features in the valence band of icosahedral $Al_{65}Cu_{20}Ru_{15}$ that could be ascribed to its quasiperiodic nature have been observed within the resolution of the experiment.

1. Introduction

Quasicrystals are a new form of matter which differs from the two well known forms, crystalline and amorphous, by possessing long-range *quasiperiodic* order and long-range orientational order of crystallographically forbidden symmetries [1, 2]. A central problem in condensed-matter physics is to determine whether quasiperiodicity leads to physical properties significantly different from those of crystalline and amorphous solids. In particular, the electronic structure of quasicrystals is of great current interest [3] as its knowledge is fundamental to our understanding of other physical properties.

Prior to 1987, all known quasicrystalline alloys were thermodynamically *metastable*. They were structurally disordered as manifested in the broadening of the x-ray- or electron-diffraction peaks. Experiments performed on such alloys showed that their physical properties are similar to those corresponding to crystalline or amorphous alloys [2, 3]. A new impetus to studying the intrinsic properties due to quasiperiodicity came with the discovery of themodynamcally *stable* quasicrystals, especially the icosahedral (I) alloys Al–Cu–TM (TM = Fe, Ru, Os) [4, 5] and Al–Pd–Mn [6]. These new I alloys possess a high degree of structural perfection comparable to that found in the best periodic alloys and they exhibit some unusual behaviour [3]. Their most characteristic feature, which is unexpected for alloys formed of normal metallic elements, is the very high value of the electrical resistivity [3] and this puts them at the border of the metal–insulator transition. The anomalously high resistivity values have been attributed [7, 8] to a very low density of states at the Fermi level,

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DOS (E_F). The low DOS (E_F), in turn, may be connected with a Hume–Rothery stabilization mechanism, which is believed to occur in I alloys [3], and which places the Fermi level into a minimum of DOS. The existence of a pseudogap at E_F is predicted by theoretical analyses based on the nearly-free-electron approximation [10, 11] and by the electronic-structure calculations performed for the lowest-order crystalline approximants [12, 13]. Experiments which probe the DOS directly, such as those based on photoemission spectroscopy (PES), inverse photoemission spectroscopy (IPES), soft x-ray emission spectroscopy (SXE), and soft x-ray absorption spectroscopy (SXA), seem to indicate that such a pseudogap exists in some I alloys [14].

The majority of physical measurements have been performed so far on stable Al–Cu–Fe [2, 3, 14] and Al–Pd–Mn [9] I alloys. Fewer studies were done on Al–Cu–Ru and Al-Cu–Os I alloys. Most of the studies carried out on I Al–Cu–Ru alloys are related to their various structural aspects and were investigated by x-ray-diffraction [15–18], electron-diffraction, and high-resolution electron-microscopy [15, 19] techniques. These structural studies established that the I Al–Cu–Ru alloys, similarly to the I Al–Cu–Fe and Al–Pd–Mn alloys, are face-centred icosahedral (FCI) alloys with an enhanced degree of chemical and topological order as manifested in the disappearance of phason disorder. In contrast to the situation for I Al–Cu–Fe [20] or Al–Pd–Mn [21] alloys, no six-dimensional structural analysis has been done for the I Al–Cu–Ru alloys.

The electrical resistivity of I Al–Cu–Ru alloys was found to strongly increase with decreasing temperature [22–24], and the largest reported value is 30 000 $\mu\Omega$ cm at 4.2 K [22]. This means that the conductivity of the I Al–Cu–Ru alloys is close to the minimum metallic conductivity of about 200 Ω^{-1} cm^{-1} [25], and these alloys can be regarded as semimetals. The specific-heat measurements [22, 23, 26] indicate a very low value of the linear electronic coefficient γ; for high-quality samples, this value is only about 10% of the estimated free-electron value. This suggests a very low DOS (E_F) and was taken, together with a strong variation of γ with composition, as evidence [22, 23, 26] of the presence of a structure-induced minimum of the DOS (E_F). On the basis of the observed temperature dependence of the Hall coefficient and thermopower, it was suggested that rapidly varying structures may exist in the DOS of I Al–Cu–Ru alloys [22, 26]. The composition independence of the NMR parameters related to DOS (E_F) [27], on the other hand, is difficult to reconcile with the dependence of γ on composition [22, 26]. The possibility of the importance of the presence of disorder even in thermodynamically stable I alloys has been suggested [27] and is confirmed by the results of Mössbauer investigations [28].

The studies of the electronic structures of I Al–Cu–Ru alloys mentioned above provide indirect information on the DOS at one particular energy E_F and suggest qualitatively the presence of rapidly varying DOS. One needs, however, more complete information on the DOS, both below and above E_F, to determine the influence of quasiperiodicity on the electronic structure of these alloys. Therefore, the use of techniques such as PES, IPES, SXE, or SXA, which probe the DOS around E_F directly, is desirable. As far as we are aware, such experiments have not been performed yet on I Al–Cu–Ru alloys. In this paper we report the first results of the PES study of I $Al_{65}Cu_{20}Ru_{15}$. The purpose of this study is to determine the valence band of this alloy and to identify its features in order to assess the role of quasiperiodicity on the electronic structure.

2. Experimental details

An alloy of composition $Al_{65}Cu_{20}Ru_{15}$ was produced by arc melting in Ar of high-purity elemental constituents. It was annealed at 1173 K for 48 h in vacuum, and then cut into slices suitable for PES measurements. The details of the sample preparation are described elsewhere [5]. All the peaks in the x-ray diffraction spectrum could be indexed to the FCI structure. Photoemission spectra were collected on beamline U14A at the National Synchrotron Light Source at Brookhaven National Laboratory. The resulting overall resolution was 0.4 eV, as determined from the width of the Fermi edge and/or from the 0.40 eV separation between the resolved $2p_{3/2}$ and $2p_{1/2}$ core-level lines of the Al reference sample.

The sample was cleaned in the experimental vacuum chamber either by 1.5 keV Ar^+ bombardment for a few minutes or by gentle mechanical abrasion using an alumina scraper. No differences could be detected between the PES spectra corresponding to these two surface-treatment methods. When ion bombardment is used to clean a surface it can lead to both chemical and topographical alterations [29, 30]. This depends, however, upon the system studied and the bombardment conditions; for some alloys [31] ion bombardment does not produce any detectable surface changes. The fact that we could not detect any differences between the PES spectra obtained from the surfaces cleaned either by Ar^+ bombardment or by scraping, together with the close structural similarity between our PES spectra measured far from the Ru 4d Cooper minimum and an XPS spectrum obtained with monochromatized Al Kα radiation (1486.6 eV) of I $Al_{61.5}Cu_{25}Ru_{13.5}$ [32] lead us to believe that our surface treatment did not result in significant topographical or compositional changes of the surface. The surface cleanliness of the sample was frequently verified by monitoring the appearance of the oxide features in the PES spectra of the Al 2p core levels and/or of the valence bands [14].

The base pressure in the experimental chamber was in the high 10^{-11} Torr range. All the PES spectra presented in this paper were obtained from at least two different regions of the sample studied, and were indistinguishable within the resolution of the experiment. In order to compare the intensities of the synchrotron-radiation-based PES spectra of a given sample, several corrections have to be taken into account [9]. The measured PES spectra were corrected first for the energy dependence of the electron transmission of the electron-energy analyser. Next, they were normalized for the photon flux, and the secondary-electron contribution was subtracted in the usual way by assuming that secondary-electron background intensity at each binding energy (BE) is proportional to the total integrated signal at lower BEs. The PES spectra corrected in such a way can be compared not only with respect to their shapes but also in terms of their intensities.

3. Results and discussion

The structure of the valence band of I $Al_{65}Cu_{20}Ru_{15}$ consists of two overlapping peaks and a broad feature around BE $= -5$ eV (figure 1). The two peaks must be predominantly of Ru 4d and Cu 3d character because the Al sp spectral contribution is expected to be much smaller due to the smaller photoionization cross section for Al sp orbitals for the photon energies, $h\nu$, used [33]. In order to identify the main feature in the valence band due to the Ru 4d states, a resonant photoemission effect [34] can be employed. In this effect the ionization cross section of the outer-shell electron is enhanced as the excitation energy exceeds the threshold of an inner excitation, which for the Ru 4p→4d transition occurs at around 43 eV. Resonant PES was used in previous work to determine the Fe and Mn 3d-derived features in the valence bands of I Al–Cu–Fe [14, 35] and Al–Pd–Mn [9] alloys. It can be seen in figure 1 that, as the photon energy increases, the intensity of the BE $= -1.3$ eV feature first decreases, reaches its minimum at $h\nu = 44$ eV, and then starts

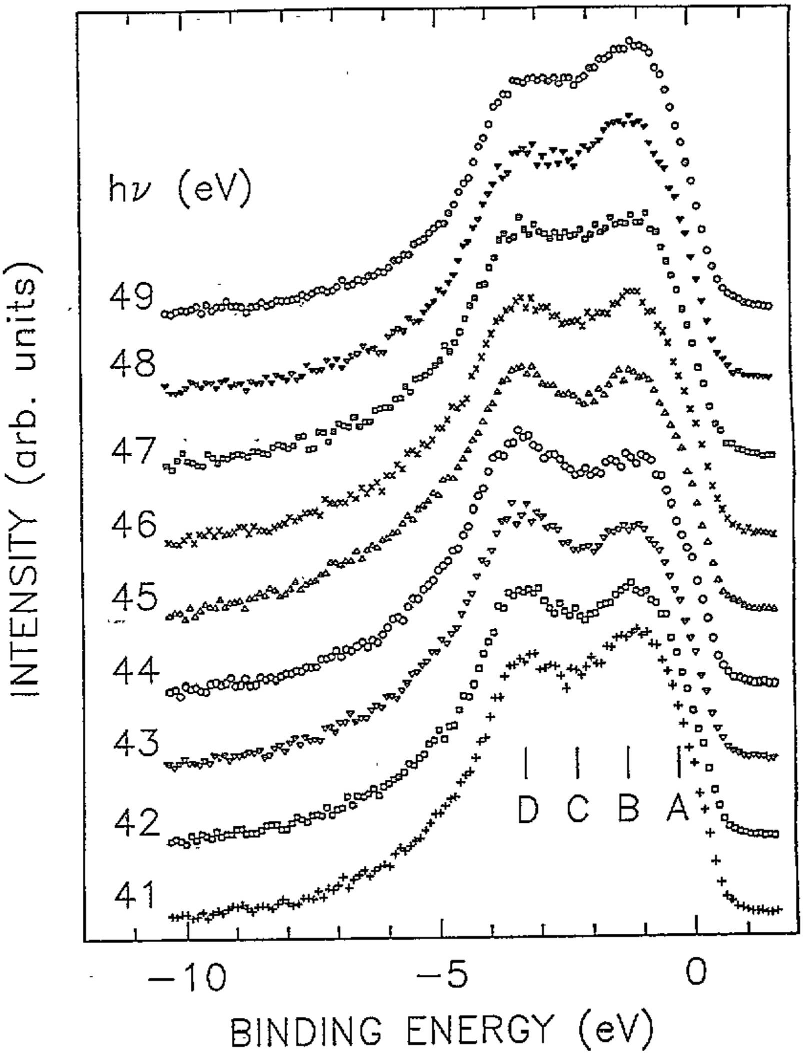

Figure 1. Valence-band spectra of the I $Al_{65}Cu_{20}Ru_{15}$ alloy measured for different photon energies *hν* around the Ru 4p→4d transition. A, B, C, and D identify binding energies for which CIS spectra were measured (figure 2).

to increase for higher values of *hν*. This indicates that this feature may be predominantly due to the Ru 4d-derived states.

Additional and more convincing evidence for associating the BE = −1.3 eV feature with the predominantly Ru 4d character can be obtained by performing a resonance experiment in the so-called constant-initial-state (CIS) mode [36]. The photoemission intensity in this mode is measured as a function of *hν* for selected valence-band positions identified by their initial energy E_i. Such CIS spectra for the E_i values corresponding to the positions denoted by A, B, C, and D in figure 1 are shown in figure 2. One can clearly see the presence of resonances for *hν* around 43 eV. The line shape of the resonance can be described by the Fano profile [34]

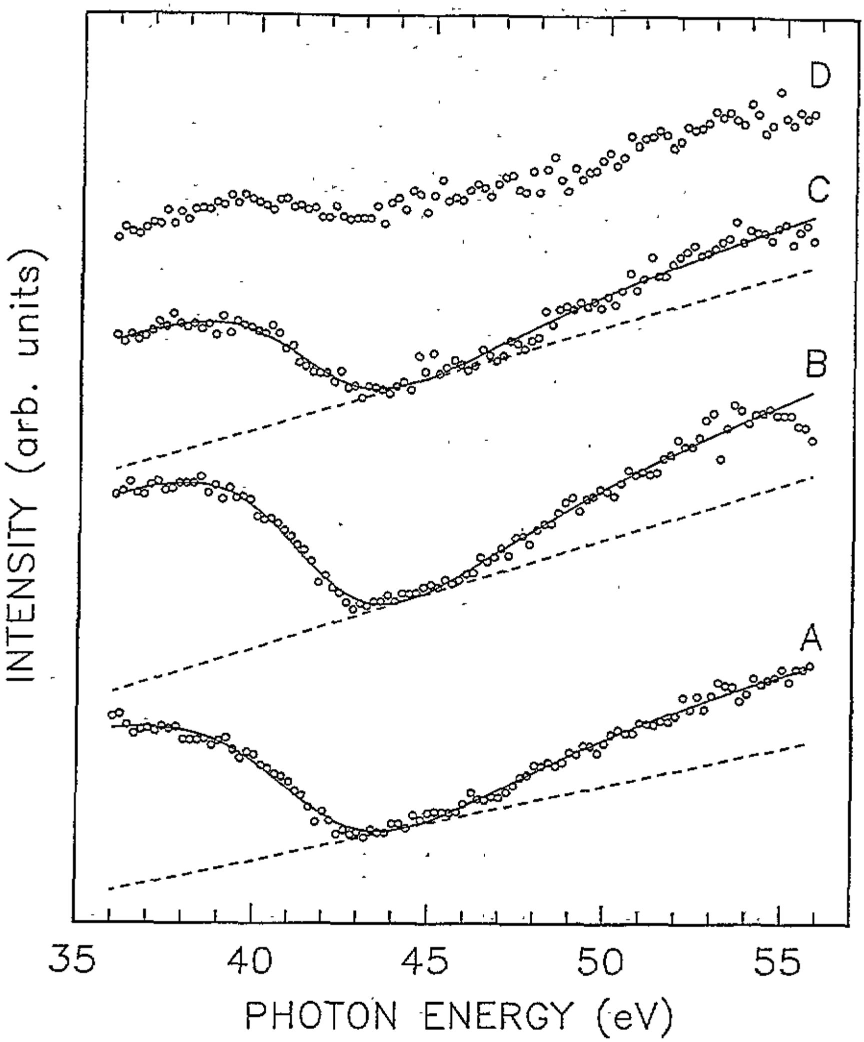

Figure 2. CIS spectra of the i $\mathrm{Al}_{65}\mathrm{Cu}_{20}\mathrm{Ru}_{15}$ alloy measured for the valence-band positions A, B, C, and D in figure 1, which are identified here by the same letters. The solid line is a fit to the Fano profile and a linear background (shown as a broken line), as described in the text and with parameters given in table 1.

$$I(h\nu) = I_0(h\nu)(\epsilon + q)^2/(1 + \epsilon^2) + I_{\mathrm{nr}}(h\nu)$$

where $I_0(h\nu)$ is the non-resonant Ru 4d emission, $I_{\mathrm{nr}}(h\nu)$ is a non-interfering background contribution, q is Fano's asymmetry parameter, and $\epsilon = 2(h\nu - E_{\mathrm{R}})/\Gamma$ is the reduced energy expressed in terms of the energy, E_{R}, and the full width at half maximum, Γ, of the resonance. A linear background was assumed in the fit (broken line in figure 2). The parameters obtained from the fit are given in table 1. The strongest resonance (the largest I_0 in table 1) occurs for $E_{\mathrm{i}} = -1.3$ eV and the resonance extends up to about -3.3 eV. This means that the maximum intensity of the Ru 4d-derived states is at around BE $= -1.3$ eV and that these states extend to lower BE values, probably due to their hybridization with the Al sp and/or Cu 3d states.

Table 1. Parameters obtained by fitting the Fano line shape to the CIS spectra in figure 2 for the E_i values corresponding to the positions A, B, and C indicated in figure 1.

E_i (eV)	I_0	E_R (eV)	q	Γ (eV)
−0.3	31.1 (1.8)	41.7 (2)	−0.58 (7)	8.9 (3)
−1.3	34.3 (1.9)	41.7 (2)	−0.68 (7)	7.8 (3)
−2.3	21.4 (2.0)	41.7 (4)	−0.72 (12)	7.6 (5)

For materials containing one of the 4d and 5d elements it is possible to separate overlapping contributions to valence bands by making use of the Cooper minimum in the photoionization cross section [37]. The decrease of the photoionization cross section of such an element in the 50–200 eV photon energy range is as large as two orders of magnitude [33, 37], making it possible to significantly decrease the emission from that element. The Cooper minimum in the Ru 4d photoionization cross section is calculated to be at $h\nu = 100$ eV [33], but is expected to occur at higher photon energies due to solid-state effects [37]. Figure 3 shows that as $h\nu$ increases from below the Cooper minimum, the relative contribution of the BE = −1.3 eV feature with respect to the other feature due to the Cu 3d states dramatically decreases, reaches its minimum at $h\nu = 130$ eV, and starts to increase for higher photon energies. The contribution due to the Cu 3d-derived states is well separated for $h\nu = 130$ eV from the contribution due to the Ru 4d-derived states (figure 3), and has its peak at BE = −3.8 eV. The weak and broad spectral weight at BE = −5 eV can be ascribed to the Al sp-derived states, based on the results of the SXE studies of I Al-based alloys [38].

It is not possible to compare the valence band of the I $Al_{65}Cu_{20}Ru_{15}$ alloy with the valence bands of the corresponding crystalline alloys since no ternary Al–Cu–Ru compounds have been reported yet [18]. The position of the maximum of the Cu 3d feature at BE = −3.8 eV is close to the corresponding position at BE = −4.3 eV in the crystalline Al_2Cu alloy [39, 40], and follows a general tendency of shifting towards more negative BEs with respect to the position at BE = −2.3 eV in pure Cu with increasing Al content [41]. Such a large shift will generally contribute to the decrease of the Cu 3d contribution to the DOS (E_F). On the other hand, the position of the maximum of the Ru 4d feature in the valence band of I $Al_{65}Cu_{20}Ru_{15}$ at BE = −1.3 eV is closer to E_F than the corresponding position at BE = −1.8 eV in pure Ru. There seem to be no PES data on the valence band in crystalline Al_2Ru. However, calculations of the DOS in this alloy indicate that the maximum of the Ru 4d contribution is at BE $\simeq -1.1$ eV and that a pseudogap of width 0.14 eV is opening up in the region of the unoccupied DOS just above E_F [42]. We can conclude that the positions of the maxima of the Cu 3d and Ru 4d features in the valence band of the I $Al_{65}Cu_{20}Ru_{15}$ alloy do not deviate from what is observed in crystalline alloys, and thus that quasiperiodicity does not seem to have a significant effect on the electronic structure.

The strong depression of intensity as the energy approaches E_F observed in the PES [14, 35] and SXE [38] spectra of the I alloys with transition-metal elements, and also observed here (figures 1 and 3), has been interpreted as evidence for the opening of a theoretically predicted [10–13] pseudogap at E_F. It is worth noticing, however, that there are two effects that lead to the intensity decrease as the energy approaches E_F. The first one is a simple Fermi cut-off, which is expected to be especially important for the alloys with elements whose d states contribute to the measured intensity close to E_F. The second effect could be associated with the opening of a pseudogap at E_F. We are only able to conclude that our PES results are indicative of a possible opening of a pseudogap at E_F in I $Al_{65}Cu_{20}Ru_{15}$. Based on the electronic-structure calculations for crystalline Al_2Ru [42], a pseudogap is

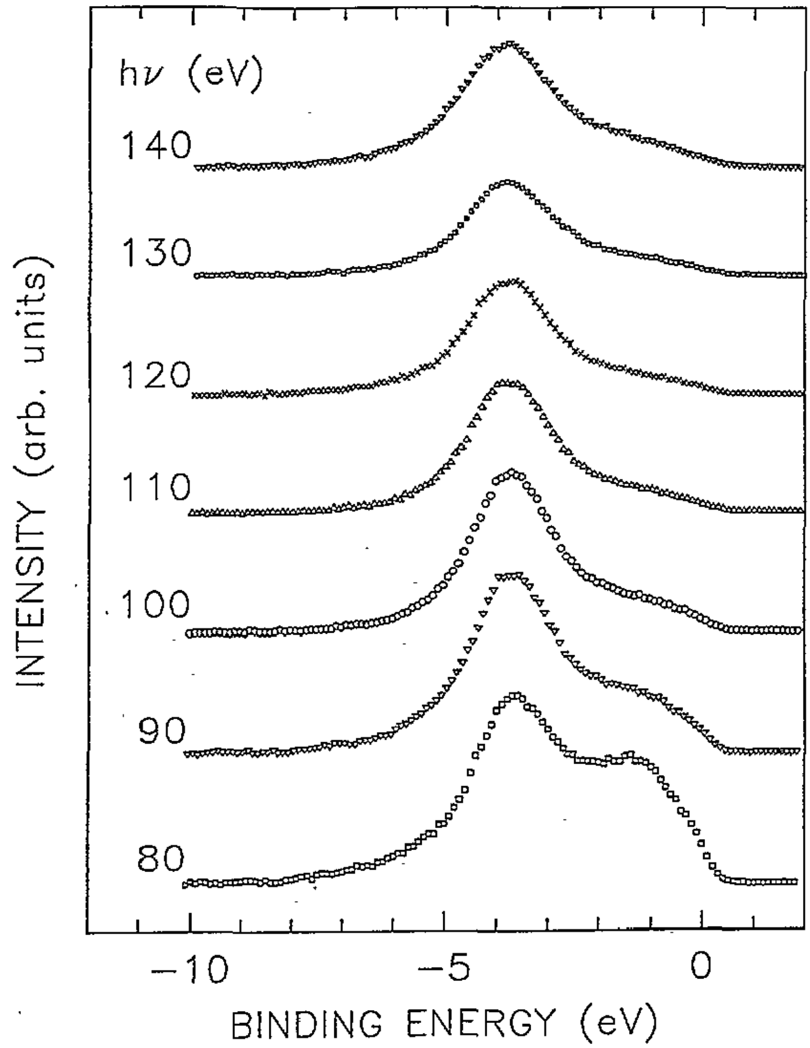

Figure 3. Valence-band spectra of the I $Al_{65}Cu_{20}Ru_{15}$ alloy for different photon energies $h\nu$ in the vicinity of the Ru 4d Cooper minimum.

expected in the unoccupied states directly above E_F rather than in the occupied states. High-resolution PES and IPES experiments are required to definitely resolve the problem of its possible existence in the I $Al_{65}Cu_{20}Ru_{15}$ alloy.

Theoretical calculations [10–13] suggests the presence of many spikes in the DOS of I alloys, which are believed to be an electronic signature of quasiperiodicity. The valence bands of I $Al_{65}Cu_{20}Ru_{15}$ presented here show no evidence for the presence of such spikes within the resolution of the experiment. These spikes have not been detected either in the PES [9, 14, 35] or SXE [38] experiments. If such spikiness indeed occurs in I alloys, it must be at an energy level much smaller than 0.1 eV. The failure to detect the spikes may be connected [26] to the presence of chemical disorder [28] in the ternary I alloys investigated in these experiments.

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