

Role of Fe and sign reversal of the Hall coefficient in quasicrystalline Al-Cu-Fe

P. Lindqvist, C. Berger, T. Klein, P. Lanco, and F. Cyrot-Lackmann
LEPES-CNRS, Boîte Postale 166, 38042 Grenoble Cedex 9, France

Y. Calvayrac
CECM-CNRS, 15 rue G. Urbain, 94407 Vitry Cedex, France
(Received 25 February 1993)

Electronic transport properties were measured for the stable icosahedral phase of Al-Cu-Fe for a large number of high-structural-quality samples of different compositions. At low temperature, the Hall coefficient R_H and the conductivity σ are found to best correlate with the Fe content rather than with the electron per atom parameter which is usually used; R_H changes sign at a concentration of 12.5 at. % Fe, where σ is at minimum. R_H has a strong temperature dependence and can change sign with temperature. These features put the focus on the Fe d states and can be interpreted by a Hume-Rothery type of behavior including the $sp-d$ hybridization effects.

The origin of the unusual electronic properties measured in high-structural-quality quasicrystalline (QC) systems is a debated and puzzling question. Low electrical conductivities, strong temperature or composition dependences of the transport properties (conductivity, Hall effect, thermoelectric power), anomalous optical conductivity, low electronic densities of states, and diamagnetic susceptibility were observed either in the icosahedral phases (i phase) of Al-Cu-Fe,^{1,2} Al-Cu-Ru,²⁻⁴ or Al-Pd-Mn.⁵ Even changes in sign with temperature in the Hall coefficient and the thermoelectric power were found in i -Al-Cu-Ru.^{2,4} It is suggested that quasicrystalline phases are stabilized, similarly to Hume-Rothery alloys, by the interaction of the pseudo-Brillouin zone boundary (of vector $K/2$) with the electron states at the Fermi level (of wave vector k_F).⁶ This gives rise to a depression in the electronic density of states at the Fermi level with a pseudogap for $K \approx 2k_F$. Within this scheme, one finds the Fermi surface is composed of electrons and hole pockets controlled by the relative position of k_F and $K/2$.⁷

Further, for the transport properties it is necessary to consider the nature of the electron states at the Fermi level as well. First, the possible existence of a new type of states, known as critical states in the case of perfect quasiperiodic tilings, may have profound consequences. The observed low conductivity (σ) values and anomalous temperature dependences $\sigma(T)$ were recently presented and discussed with this idea.⁸ Second, the $s-p$ or d character of the states at the Fermi level have also to be considered for the transport properties because of their expected different mobilities. The role of the transition metals (TM) is not yet clarified but is of importance, as is, for instance, outlined by the thermodynamical stability of i -Al-Cu-Fe, whereas i -Al-Cu-Mn is metastable. It is known from x-ray spectroscopic measurements in i -Al-Cu-Fe (Ref. 9) that Fe d states are present at the Fermi level and are strongly hybridized with the sp states. As a consequence the sp band is strongly modified, and it has been recently shown by calculations on Al-MT crystals that this $sp-d$ hybridization effect tends to deepen the

pseudogap at E_F . Therefore, the Hume-Rothery picture, which was initially developed for sp compounds and extended to alloys containing TM,¹⁰ can also describe i -Al-Cu-Fe phases,^{11,12} with a pseudogap enforced by the presence of the d states at E_F .

In this paper we show the importance of the d states for the conductivity σ and Hall effect R_H of high structural quality i -Al-Cu-Fe alloys. The variation of σ and R_H indeed best correlate with the Fe concentration rather than with the usual electron per atom parameter. We find that the sign reversal of R_H coincides with the minimum of σ . We also show that R_H changes sign with temperature for the lowest conducting i -Al-Cu-Fe samples. We propose that an anomalous dispersion relation $E(k)$ induced by $sp-d$ hybridization effects may be at the origin of these behaviors.

We carefully tuned the composition around $\text{Al}_{62.5}\text{Cu}_{25.5}\text{Fe}_{12.5}$ over the whole (but small) formation range where icosahedral i -Al-Cu-Fe alloys have their lowest conductivities¹ and highest stability.¹³ The rapidly quenched samples were annealed at 800 °C in order to obtain pure i - $\text{Al}_{100-x-y}\text{Cu}_x\text{Fe}_y$ alloys of high structural quality in the ranges $24.4 \leq x \leq 26.0$ and $12.0 \leq y \leq 13.0$. We checked that the conductivity results are reproducible between different pieces of samples of the same batch or taken from different quenches or produced in two different laboratories (LEPES or CECM), or samples in the form of ribbons, ingots, or single grains (for $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$). The measurement methods are described elsewhere;¹ R_H was measured from 4.2 K to room temperature, and σ is taken at 4.2 K. The absolute values were determined with an accuracy of about $\pm 10\%$, where the main errors come from geometrical factors. We observe no deviations from linearity with fields up to 5 T for the Hall resistivity $\rho_H = R_H H$. That is in agreement with the diamagnetic character of the i -Al-Cu-Fe phase.¹⁴

We observe strong variations in the values of σ and R_H by varying concentration. This is remarkable in view of the small concentration range allowed for the study. At

4.2 K, σ is spanning over the range 95–260 ($\Omega \text{ cm}$)⁻¹. This means an extreme sensitivity to the composition which has been interpreted by the proximity of the metal-insulator transition.¹ As for R_H , not only the magnitude but also the sign are very sensitive to composition: R_H varies from -2.1×10^{-8} to $+9.4 \times 10^{-9}$ m³/As as the Fe concentration is increased. The absolute values are large and correspond to very low effective numbers of carriers: $n_{\text{eff}} = (eR_H)^{-1} \sim 5 \times 10^{20}$ cm⁻³. This is only about 1/100 of the free electron value, and is of similar magnitude as *i*-Al-Cu-Ru.² But in our case these low values are not simply related to the density of states. Indeed, the electronic term of specific heat γ is almost the same for all the measured *i*-Al-Cu-Fe, and is small [$\gamma \sim 0.3$ mJ/mol K² (Refs. 1, 2, and 15)]. This value corresponds to $\frac{1}{3}$ of the estimated free electron value, and does not agree with the free electron relation $n_{\text{eff}} \sim \gamma^3$. On the other hand, in a simple two-band scheme like the one implied by the Hume-Rothery picture, these low values indicate a good compensation between electrons and holes [the free electron description of two contributing bands gives $R_H = 1/en_{\text{eff}} = (1/e)(p\mu_h^2 - n\mu_e^2) / (p\mu_h + n\mu_e)^2$, with n and p the number of electrons and holes, respectively, and μ the corresponding mobility of the carriers].

We first plot our transport data versus the average number of electrons per atom e/a . This ratio is often taken as a good quantity for the size of the Fermi sphere. Within a Hume-Rothery picture, this could hence probe the pseudogap when composition is varied. In *sp* quasicrystals like *i*-Al-Cu-Mg, anomalies in the electric properties have been found for each e/a value for which the condition $K \sim 2k_F$ is fulfilled.² In Fig. 1 we show R_H of *i*-Al-Cu-Fe as a function of e/a as calculated from the valencies +3 for Al, +1 for Cu, and an effective negative valency -2 for Fe that takes the *d* states into account. The e/a plot is not at all conclusive since positive and negative values overlap. In the inset of Fig. 1 a simple

correlation for σ vs e/a does not work well either, although the lowest conductivities all lie in the same e/a range.

Several problems could affect these plots. First is the choice of the valency for Fe (e/a)_{Fe}. As shown by recent calculations¹¹ on crystalline Al transition metal, the apparent negative values may result from hybridization of the *sp* band with the *d* band [it is then found that $(e/a)_{\text{Fe}} \sim -1.5$ (Ref. 11)], rather than due to a charge transfer as proposed earlier by Pauling [$(e/a)_{\text{Fe}} = -2.66$ (Ref. 16)]. For Fig. 1, we chose a reasonable value of $(e/a)_{\text{Fe}} = -2$, but the plots are equally bad for $(e/a)_{\text{Fe}} = -1$, or -3 . Small variations of the Fe valency cannot be ruled out, since by changing composition, one also changes the relative number of coupled *d* and *sp* states. Also, different effective valencies may have to be considered if Fe atoms occupy different sites in the QC structure. Second, the total allowed variation for e/a is very small [$\Delta(e/a) \sim 0.04e/\text{at.}$], which is perhaps not sufficient to observe variations in the properties [for instance in *i*-Al-Cu-Mg, $\Delta(e/a) \sim 0.4e/\text{at.}$].

As shown in Fig. 2, we instead found a very good correlation between the σ and R_H data and the Fe content, whereas no correlation is observed between σ or R_H and Al or Cu. In Fig. 2, σ presents a minimum as low as ~ 100 ($\Omega \text{ cm}$)⁻¹ at 12.5 at. % Fe for the concentration value where R_H abruptly changes sign from negative to positive. The 12.5 at. % Fe value can thus be considered to be a critical line, for which the *i*-Al-Cu-Fe samples are the closest to the metal-insulator transition, and with the best electron-hole compensation. At this point (12.5 at. % Fe) the properties are very sensitive to composition, which again indicate the proximity of a transition: for instance for *i*-Al_{62.5}Cu₂₅Fe_{12.5}, the magnitude of the Hall effect (not the sign) can vary considerably between different pieces of ribbons. Moreover for *i*-Al₆₃Cu_{24.5}Fe_{12.5} (No. 10), that contains the highest amount of Al in the series, the σ value deviates from the

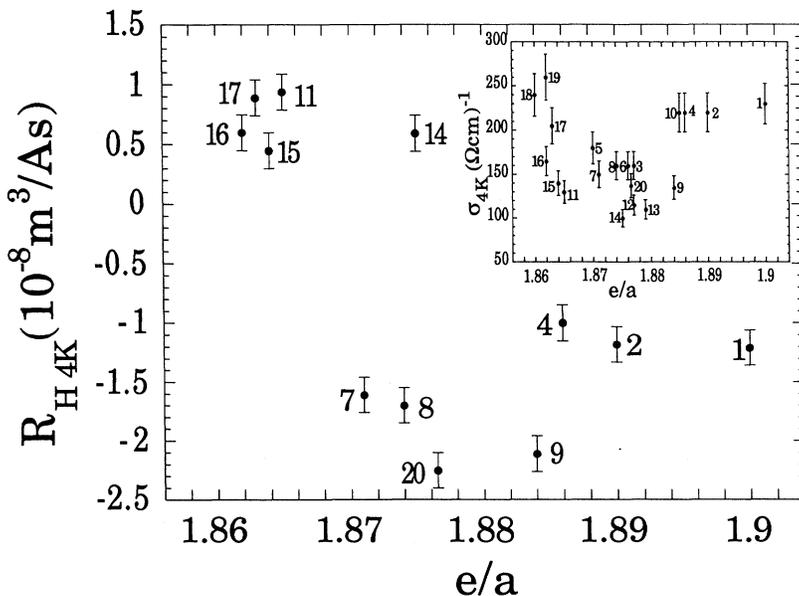


FIG. 1. The Hall coefficient vs (e/a) . Inset: the electrical conductivity vs (e/a) . The numbers indicate samples as follows: (1) Al₆₃Cu₂₅Fe₁₂, (2) Al_{62.5}Cu_{25.5}Fe₁₂, (3) Al₆₂Cu_{25.9}Fe_{12.1}, (4) Al_{62.6}Cu_{25.2}Fe_{12.2}, (5) Al_{61.8}Cu₂₆Fe_{12.2}, (6) Al_{62.1}Cu_{25.7}Fe_{12.2}, (7) Al₆₂Cu_{25.7}Fe_{12.3}, (8) Al_{62.3}Cu_{25.3}Fe_{12.4}, (9) Al_{62.8}Cu_{24.8}Fe_{12.4}, (10) Al₆₃Cu_{24.5}Fe_{12.5}, (11) Al₆₂Cu_{25.5}Fe_{12.5}, (12) Al_{62.6}Cu_{24.9}Fe_{12.5}, (13) Al_{62.7}Cu_{24.8}Fe_{12.5}, (14) Al_{62.5}Cu₂₅Fe_{12.5}, (15) Al_{62.1}Cu_{25.3}Fe_{12.6}, (16) Al_{62.3}Cu_{24.9}Fe_{12.8}, (17) Al_{62.5}Cu_{24.6}Fe_{12.9}, (18) Al_{62.5}Cu_{24.5}Fe₁₃, (19) Al_{62.6}Cu_{24.4}Fe₁₃, (20) Al_{62.5}Cu_{25.05}Fe_{12.45}.

single $\sigma(\text{Fe})$ curve. This might indicate a change in composition of the local chemical order, which would have consequences on the transport properties.

Since we know that the presence of defects *reduces* the resistivity,¹ it may be that the 12.5 at. % Fe concentration corresponds to the maximum chemical order of the icosahedral structure. This point is not easy to check from our x-ray diffraction data, as we have to compare relative intensities of the superlattice x-ray peaks as a function of composition.

In Fig. 3, R_H is presented as a function of temperature for two samples of constant R_H sign (negative or positive) and the $i\text{-Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$ sample that changes sign with temperature. It is worth noting that the R_H sign reversal is for the sample of the lowest conductivity, and that is on the "critical" 12.5 at. % Fe line. At low temperature, the R_H values are only weakly temperature dependent; at very low temperature \sqrt{T} behaviors have been observed and attributed to electron-electron interaction effects.¹ But R_H varies more strongly at higher temperatures, and all three samples seem to approach a common negative value well above room temperature. Within a simple Hume-Rothery two-band picture, as seen above, the sign

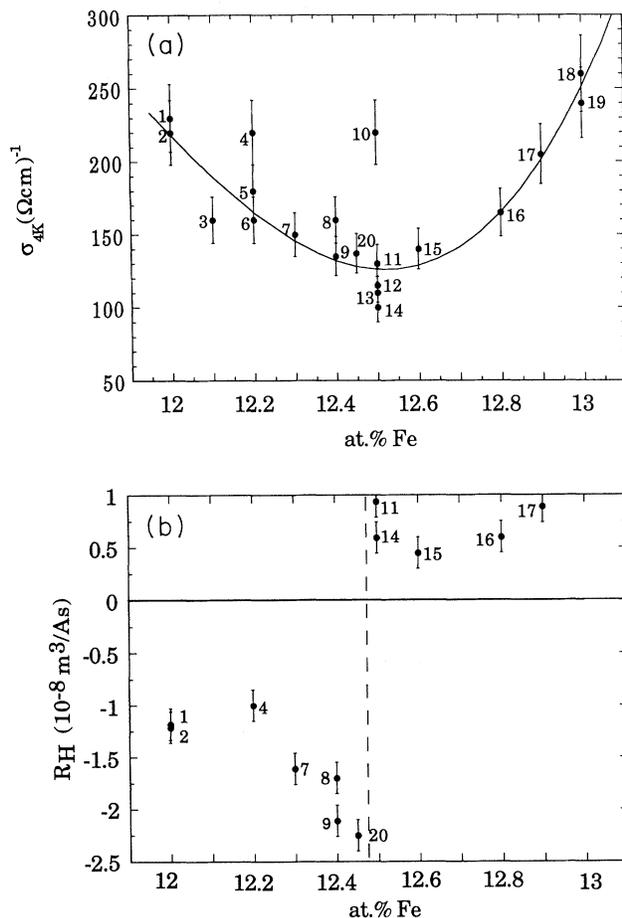


FIG. 2. (a) The electrical conductivity and (b) the Hall coefficient vs nominal Fe content for $i\text{-Al-Cu-Fe}$ samples. The sample numbers are the same as in Fig. 1.

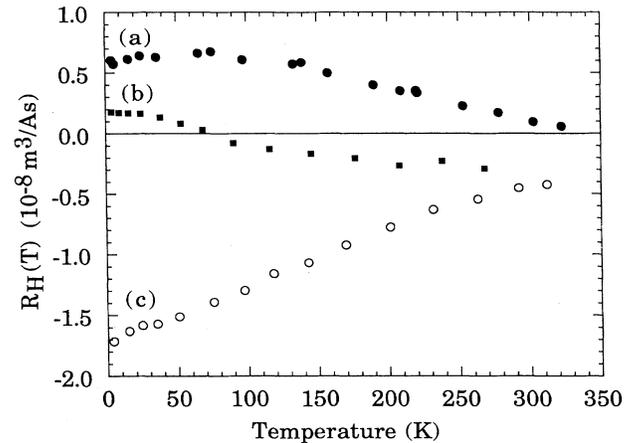


FIG. 3. The Hall coefficient vs temperature for (a) $\text{Al}_{62.3}\text{Cu}_{24.9}\text{Fe}_{12.8}$, (b) $\text{Al}_{62.5}\text{Cu}_{25}\text{Fe}_{12.5}$, (c) $\text{Al}_{62.8}\text{Cu}_{24.8}\text{Fe}_{12.4}$.

of R_H depends on the dominating type of carriers. Hence, variation of the Fermi level with composition will change the delicate electron-hole balance and give either negative or positive R_H . With different temperature dependences for the mobilities of electrons and holes, a sign reversal of R_H with temperature is also expected.

The σ and R_H dependences on the Fe concentration indicate that Fe d states have also to be considered. We first exclude the explanation for a sign reversal of R_H based on skew scattering. These effects indeed require spontaneous localized moments that are not observed in our diamagnetic $i\text{-Al-Cu-Fe}$. Further, the Hall resistivity presents no detectable curvature with field. We propose rather to describe the Hall effect by the same picture as the one developed for disordered Cu-TM systems¹⁷. In that case a sign reversal of R_H , from negative to positive, is observed by increasing TM concentration. It is correlated to a change in the atomic short-range ordering, which is there shown to be a determining parameter in the calculation of the density of states. Now, from electronic structure calculation, or more precisely the energy dispersion $E(k)$, the sign of the group velocity at E_F (and hence of R_H) could be deduced. It was thus shown that the $sp-d$ hybridization effect well described the sign reversal of R_H , through a modification of $\delta E(k)/\delta k$ at E_F induced by local atomic order.

In the case of $i\text{-Al-Cu-Fe}$, we propose that the same kind of effects may occur, and this because of several points of similarity between both types of systems. First, as for amorphous CuTM alloys, d states at E_F are strongly hybridized with sp states as mentioned above. Second, a strong chemical order exists in these i phases, as indicated by the superlattice diffraction peaks. One possibility is that this order is optimum for the precise Fe concentration (12.5 at. % Fe) for which R_H changes its sign but also σ is at minimum. There are good indications that the less defective the sample, the lower the conductivity.¹ Indeed, moderately annealed $i\text{-Al-Cu-Fe}$ phases, that still contain defects but where additional phases were not detected either by x-ray diffraction or electron microscopy, present higher conductivities than the high-quality i

phases. It is also reasonable to suppose that the local environments (say 20–30 Å) have an important role since the same unusual electronic transport features are found in *i*-Al-Cu-Fe, *i*-Al-Pd-Mn and in the approximant phases *R*-Al-Cu-Fe and α -Al-Mn-Si for σ and R_H .^{18,8} Finally, the density of states seems to be very sensitive to the Fe atomic positions, as shown in a recent model¹¹ by taking explicitly into account the *d* states, where results were confirmed by calculations on Al-TM crystals. The role of local environments is thus to be considered in *i*-Al-Cu-Fe like in the disordered case. Then *sp-d* hybridization effects at the Fermi level may be responsible for the sign reversal in R_H .

In summary, we present evidences of the role of Fe in the conductivity and Hall coefficient of *i*-Al-Cu-Fe phases. We first showed that the plot σ vs e/a is not

alone convincing, whereas a clear dependence of σ and R_H on the Fe concentration is observed, with a sign reversal of R_H corresponding to a minimum of conductivity. The presence of the transition metal thus is the dominating parameter in the relative variations of σ and R_H . Beyond the Hume-Rothery description for the electronic structure of quasicrystals, the hybridization effects between *sp* and *d* states at the Fermi levels is believed to drive the sign reversal of the Hall coefficient.

We would like to thank N. W. Ashcroft and D. Mayou for very stimulating discussions. We thank G. Fourcaudot and J. C. Grieco for technical support and for the preparation of samples. T. Klein acknowledges CEA-CEREM for financial support. P. Lindqvist is grateful for a grant from the French ministry of research.

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