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## EXAFS study of the Fe local environment in icosahedral AlCuFe and its relation to magnetism of quasicrystals

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### Abstract

An extended X-ray absorption fine structure study of the transition metal sites in an icosahedral Al<sub>63</sub>Cu<sub>25</sub>Fe<sub>12</sub> quasicrystal was performed. The nearest-neighbor coordination shell of the Fe atoms was found to contain Al atoms only, whereas the Cu atoms are surrounded predominantly by the Al atoms and some Cu atoms as the nearest neighbors, but no Fe atoms. The results give experimental support to the physical picture of Fe atoms embedded in an Al-rich environment without direct contacts to other Fe's, providing a basis for the study of unusual magnetism in transition-metal-containing aluminum-based quasicrystals. © 2002 Elsevier Science Ltd. All rights reserved.

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The anomalous magnetic properties of transition-metal-containing aluminum-based quasicrystals (QCs) represent a major open issue in the context of magnetism in quasiperiodic structures, for a review see Ref. [1]. Experimentally most-studied examples are the icosahedral *i*-AlPdMn and *i*-AlCuFe families, where unpaired d electrons of the Mn and Fe atoms introduce localized magnetic moments. The astonishing feature here is that only a small fraction of transition-metal atoms carry magnetic moments, i.e. of the order 1% of all Mn atoms in the *i*-AlPdMn and 10<sup>-4</sup> of all Fe atoms in the *i*-AlCuFe, the rest being nonmagnetic. A similar situation was found also in other quasiperiodicity-related aluminum-rich systems, like the metastable Al(Si)-Mn QCs and some stable approximants ( $\mu$ -Al<sub>4</sub>Mn, Mn-rich Taylor phase, and 1/1 Al-Pd-Mn-Si). In contrast, Mn atoms are nonmagnetic in most periodic crystalline Al-rich phases and become largely magnetic in the liquid state above the melting point of both, crystals and QCs [2].

In order to explain the marginal magnetism of Mn- and

Fe-containing Al-based QCs and their approximants, several theoretical approaches were examined. Most studies of the magnetic moment formation have focused on the role of the local chemical environment at different inequivalent lattice sites. Ab initio calculations of the local electronic density of states [3] for the AlPdMn periodic approximants demonstrated that the local atomic coordination around a given Mn site allows the formation of moments only on a small number of Mn sites that are characterized by a loose coordination of Al atoms and some close Pd neighbors, but no close Mn neighbors. Direct Mn-Pd contacts, which exist in a substantial number only on a few Mn sites, lead to a locally enhanced Mn-d-Pd-d hybridization and repulsion between the nearly full Pd-d band and the half-filled Mn-d band, thus promoting the moment formation.

In a quite different approach it was argued that an effective, medium-range Mn-Mn interaction mediated by the conduction electrons plays a major role in the formation of Mn moments [4] in the *i*-AlPdMn. A general interaction between Mn atoms that are embedded within an Al-rich environment, but are not nearest neighbors, was derived. The interaction energy of two Mn atoms separated by a distance *r* and being either nonmagnetic or carrying

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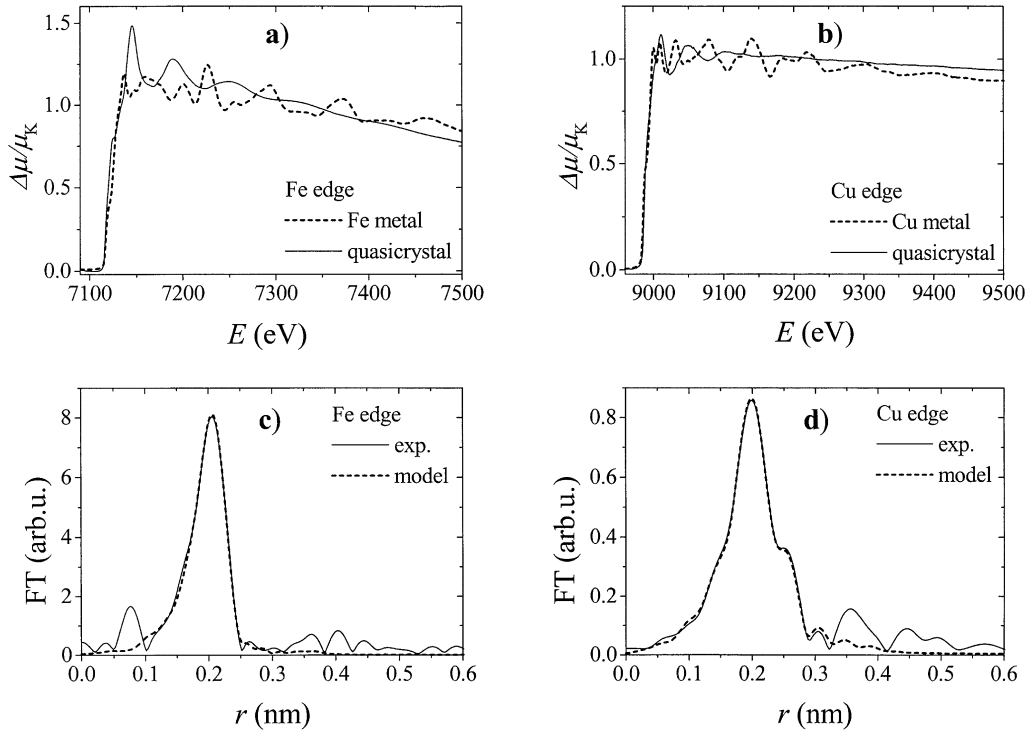


Fig. 1. (a) The normalized near-K-edge EXAFS absorption signal of the icosahedral  $\text{AlCuFe}_{12}$  at the Fe edge (solid line) compared with the respective signal of an Fe metal (dotted line), and (b) the respective signal at the Cu edge (solid line) compared with a Cu metal (dotted line). (c) and (d) show the corresponding FTs of the above EXAFS signals (solid lines) together with the fits (dotted lines) obtained by the FEFF model.

magnetic moments  $\bar{\mu}_1$  and  $\bar{\mu}_2$  was shown to obey a general form

$$E_2(r, \bar{\mu}_1, \bar{\mu}_2) = a(r) + \frac{b(r)}{2}(\mu_1^2 + \mu_2^2) + c(r)\bar{\mu}_1 \cdot \bar{\mu}_2 \quad (1)$$

The  $a(r)$  term is the electrostatic potential energy between the two nonmagnetic Mns, which oscillates with distance (Friedel oscillations), whereas the  $c(r)$  term corresponds to a RKKY (Ruderman–Kittel–Kasuya–Yosida) interaction between moments. The term  $b(r)$  plays a central role in the formation of local magnetic moments. Even if atom 2 has a zero moment it modifies the electronic structure around atom one and changes its magnetic energy that can result in moment formation at a particular lattice site. Due to  $b(r)$ , the formation of a moment on an Mn atom is sensitive to the proximity of other nonmagnetic Mn's. The coefficients  $a(r)$ ,  $b(r)$  and  $c(r)$  are obtained by a numerical calculation for a particular crystallographic structure of an approximant phase. In real alloys this medium-range Mn–Mn interaction is affected by finite mean-free path  $l_0$  of the conduction electrons due to scattering by static disorder or phonons. The interaction between atoms that are separated by a distance  $r$  larger than  $l_0$  is affected by scattering and leads to an exponential damping of the form  $b(r) \exp(-r/l_0)$ . Numerical simulations for several approximants correctly reproduced the experimental fact that only a

tiny fraction of Mn sites are magnetic. Moreover, for particular Mn sites the calculation also predicts a transition from a magnetic to a nonmagnetic state in case when a temperature-dependent mean-free path  $l_0$  gets shorter than a characteristic length related to the Mn–Mn separation distance. Since QCs typically exhibit a negative-temperature-coefficient electrical resistivity that can be associated with a decreasing  $l_0$  upon cooling, this may result in further reduction of the magnetic Mn fraction at low temperatures.

Still another explanation of the nonmagnetic character of most of the Mn and Fe sites in QCs was given in terms of the Kondo effect. A recently reported temperature-dependent magnetic susceptibilities [5] of  $i\text{-AlPdMn}$ , decagonal  $\text{AlMnFeCr}$  and periodic hexagonal  $\mu\text{-Al}_4\text{Mn}_x\text{Cr}_{1-x}$  phases could be consistently explained by the Kondo screening of moments that occurs below a Kondo temperature of the order of 1 K. The existence of the Kondo effect in Al-based QCs could be anticipated by comparing these systems to the related Al-rich crystalline alloys. It is well known that diluted Mn and Fe atoms in Al–Mn, Al–Fe or Cu–Fe alloys are Kondo-compensated. In Al–Mn, manganese atoms remain nonmagnetic up to 1000 K [6], whereas in Cu–Fe the Kondo compensation occurs below 10 K. However, the existence of Kondo effect in Al-based QCs does not appear trivial. It was argued [7] that the Kondo-type screening of moments by conduction electrons in QCs could not take

Table 1

Best FEFF fit parameters for the Fe target atom at the K edge. The parameter  $\Delta r(\text{Al})$  is the adjustment of the nearest-neighbor Fe–Al distance against the sum of the metal radii (obtained from tabulated data as  $r(\text{Fe–Al}) = 0.24792$  nm),  $n(\text{Al})$  is the number of Al atoms in the nearest-neighbor shell and  $\sigma(\text{Al})$  denotes the width of the distribution of the nearest-neighbor Fe–Al distances

Variable	Best fit	Value uncertainty
$\Delta r(\text{Al})$ (nm)	–0.019	0.0003
$n(\text{Al})$	5.9	0.21
$\sigma^2(\text{Al})$ (nm) <sup>2</sup>	$1 \times 10^{-4}$	$4 \times 10^{-6}$

place because of the low density of electronic states at the Fermi energy.

The above three models of the moment formation in Al-based QCs are not easy to discriminate on the basis of available experiments. It is not clear whether one of these can be considered as generally valid for QCs or a proper explanation is sample-dependent, i.e. it depends on the sample composition and its structural perfection. In addition, none of the theoretical models mentioned earlier is QC-specific, but all represent extrapolation of theories valid for periodic crystals. Due to the fundamental difference in the conduction electron states between QCs and regular metals—the states in QCs are critical, i.e. localized on a scale over many interatomic distances, instead of being extended as in regular metals—this extrapolation is far from being trivial. However, common to all the models mentioned earlier is the assumption that the transition metal atoms (Mn, Fe) are embedded in an aluminum-rich environment with predominantly Al atoms as the nearest neighbors, but no direct contact to other transition metals, so that they act in a way as impurities in an Al metallic host matrix. In order to give further consideration on the applicability of these models to QCs, we performed an EXAFS (extended X-ray absorption fine structure) study of an *i*-AlCuFe sample with the aim to determine the local environment of the Fe atoms and, in particular, to find experimentally whether there exist direct contacts between the Fe atoms.

The EXAFS study was performed on a polygrain icosahedral  $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$  QC sample (referred in the following as AlCuFe<sub>12</sub>), for which an X-ray diffractogram showed a perfect icosahedral state. In the *i*-AlCuFe, Fe atoms (spin  $S = 2$ ) [8] play the role of magnetic atoms analogous to Mn in the *i*-AlPdMn and these two QC families are also isostructural. The EXAFS technique is based on a diffraction of a photoelectron on the atoms in the immediate neighborhood of the target atom. The interference of the diffracted photoelectron wave with the emitted wave is recorded in a small oscillatory component of the X-ray absorption cross-section in the energy region above a major absorption edge (K or L). The analysis of the EXAFS signal yields chemical species of the neighboring atoms, their distances to the target atom and the spread of the distances,

either due to thermal motion or to static disorder of atomic positions. A few shells of closest neighbors can be discerned; of the order 10 for perfect periodic crystals, and 1 or 2 for amorphous phases. In *i*-AlCuFe QCs one should thus be able to determine the nearest environment of the Fe atoms.

The experiment was performed at the HasyLab E4 station at the DORIS ring of DESY, Hamburg. The K edge EXAFS signal of Fe (7111 eV) and Cu (8981 eV) on a powdered AlCuFe<sub>12</sub> sample was measured in a series of scans. In parallel with the QC sample, the absorption of respective pure metals (Fe, Cu) was measured on the same beam, providing absolute energy calibration. The measured absorption spectra, averaged over 5 scans, are shown in Fig. 1(a) and (b). The initial information on the target atoms in their particular environment is obtained by the inspection of the near-edge region (XANES). The comparison of K edges in the AlCuFe<sub>12</sub> and the pure metals shows that the position of the Fermi level, concurrent with the point of the steepest increase of the edge profile, is practically unchanged in Fe and possibly shifted for less than 1 eV in Cu. This means that the ‘chemical’ state of the two elements (i.e. the effective ionic charge) in the quasicrystalline alloy is practically the same as in pure metallic phases. The site symmetry in the QC alloy is, however, completely changed as evidenced from the EXAFS oscillations above the edge. Fourier transforms (FT) of the EXAFS signals are displayed in Fig. 1(c) and (d). The position of a peak in FT is related to the distance between the target atom and its respective neighbor while the peak area corresponds to the occupation of the neighbor shell. The width of the peak is a direct measure of the spread of the distances. In both FT graphs we observe a prominent peak at or just above 0.2 nm, the contribution of the first neighbor shell. Further peaks, more evident in Cu, denote farther neighbors. From the rapid decrease of the peak size we conclude that the farther shells are considerably less well defined so that the signal averages out close to zero. Accordingly we can expect reliable parameters for the first neighbors. The analysis then proceeds with the FEFF model [9,10], where the candidate neighbors (Al, Cu and Fe) of each target atom (Fe and Cu) are placed at distances, which are sums of the respective metallic radii from tabulated data. The model of the interval 0.11–0.32 nm, corresponding to the region of the first neighbor shell, leads in both cases to a very satisfactory agreement (dashed lines in Fig. 1(c) and (d)). For the Fe target atom, the best FEFF fit (Table 1) retains a single species only—the aluminum atoms—in the first coordination shell. Models, which include Cu and/or Fe atoms among first neighbors, are rejected with statistical significance. The Fe–Al distance is by 0.019 nm smaller than the sum of metal radii (obtained from tabulated data as  $r(\text{Fe–Al}) = 0.24792$  nm), which is a rather strong contraction, probably due to partial loss of electrons from Al, converting it to a smaller ionic state. The number of Al neighbors is close to 6 ( $5.9 \pm 0.2$ ). The width of the distribution of

Table 2

Best FEFF fit parameters for the Cu target atom at the K edge. The parameter  $\Delta r(\text{Cu})$  is the adjustment of the nearest-neighbor Cu–Cu distance against the sum of the metal radii ( $r(\text{Cu–Cu}) = 0.25698$  nm) and  $n(\text{Cu})$  is the number of Cu atoms in the nearest-neighbor shell. The quantities  $\Delta r(\text{Al})$  and  $n(\text{Al})$  are the corresponding parameters for the Al nearest neighbors of the target Cu atom (the sum of the metal radii here amounts to  $r(\text{Cu–Al}) = 0.25561$  nm). The parameter  $\sigma(\text{Al})$  denotes the spread of the Cu–Al distances; the corresponding parameter for the Cu–Cu distances could not be determined due to a high correlation with  $\Delta r(\text{Al})$

Variable	Best fit	Value uncertainty
$\Delta r(\text{Cu})$ (nm)	0.001	0.0008
$\Delta r(\text{Al})$ (nm)	–0.015	0.0006
$n(\text{Cu})$	0.36	0.04
$n(\text{Al})$	5.8	0.32
$\sigma^2(\text{Al})$ (nm) <sup>2</sup>	$1.9 \times 10^{-4}$	$2 \times 10^{-5}$

distances is large,  $\sigma^2 = 1 \times 10^{-4}$  (nm)<sup>2</sup> (for pure metals it is rather about  $2 \times 10^{-5}$  (nm)<sup>2</sup>), so that the spread of the distances is about 0.01 nm, reflecting the variety of neighborhoods comprised in the quasiperiodic lattice. For the Cu target atom (Table 2), only the Al and Cu neighbors are accepted in the FEFF fit. Again, Fe neighbors are excluded with statistical significance. The Cu–Cu distance is close to that in Cu fcc metal, whereas the Cu–Al distance is again contracted by 0.015 nm. There are again almost six Al atoms in the first neighbor shell, but also about 0.4 Cu. The spread of the Cu–Al distances is again quite high (0.014 nm), even bigger than for the Fe–Al distances.

The above EXAFS results clearly demonstrate that the first coordination shell of the Fe atoms in the AlCuFe<sub>12</sub> contains a single species only—the aluminum atoms—thus supporting the physical picture of the transition metal atoms embedded in an Al-rich environment without direct contacts to other transition metals. From the theoretical side, this is the basic assumption underlying the above-discussed theoretical models—the medium-range Mn–Mn interaction

including the RKKY coupling, the Kondo theory of screening and the ab initio calculation of the local density of states—employed to describe magnetism in transition-metal-containing Al-based QCs. Though these models are not QC-specific, but represent extrapolation of theories valid for periodic crystals, the above EXAFS study gives some confidence to use them as a starting point to describe magnetism in QCs, at least on a qualitative level. However, due to a fundamental difference between the electronic properties of QCs and periodic alloys, a complete theory of magnetism in QCs is still to be obtained.

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