Magnetic properties and the electronic structure of a stable Al-Cu-Fe icosahedral phase

LETTER TO THE EDITOR

Magnetic properties and the electronic structure of a stable Al–Cu–Fe icosahedral phase

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Abstract. The stable Al–Cu–Fe icosahedral phase showed almost no local magnetic moment at low temperatures, and a dependence of the magnetic susceptibility linear to the square of the temperature above about 150 K. The former is interpreted by the condition of the local magnetic moment formation according to the theory of Friedel and Anderson, and the latter affords strong experimental evidence for the band gap corresponding to the Brillouin zone inferred for strong diffraction spots. An experimental value of the mass density is obtained, in order to estimate the electron number density.

Theoretical investigations predicted that the quasicrystal would show various interesting electronic properties. Investigations showed energy spectrum to have strong van Hove singularity [1], the self-similar property [2] and the 'critical' behaviour in the localisation characteristic [3] of some of the wavefunctions obtained by the use of the tight-binding scheme for two-dimensional Penrose tiling. The energy spectrum of the three-dimensional quasicrystal, the icosahedral phase, does not yet seem to have been calculated in as full detail as was the 2-dimensional case, even for the simple tight-binding scheme. The remarkable point that diffraction spots are very sharp and strong in spite of the lack of translation symmetry [4] seems to attract less attention than do the electronic properties in such calculations, at least in an explicit way. More detailed theoretical calculation of the electronic structure of the 'real' three-dimensional icosahedral phase may be difficult at present, because neither an atomic structure model—that is, an arrangement for each constituent atom–nor a powerful framework such as Bloch's theorem is at present established. Some reasonable approximate methods, if feasible, might be useful in interpreting experimental results, in view of the present states of theoretical studies.

Recently, high-temperature magnetic properties of a stable Al–Cu–Fe icosahedral phase have been investigated [5]. A linear relationship was found between the magnetic susceptibility (χ) and the square of temperature (T^2), which suggested a particularly sharp valley-like structure in the electronic density of states (DOS) at the Fermi energy (E_F) on interpreting the T^2 dependence as a consequence of the temperature dependence of Pauli paramagnetism [5]. The present Letter gives an elementary interpretation of the T^2 dependence on the basis of the electronic structure inferred from the strong diffraction spots.
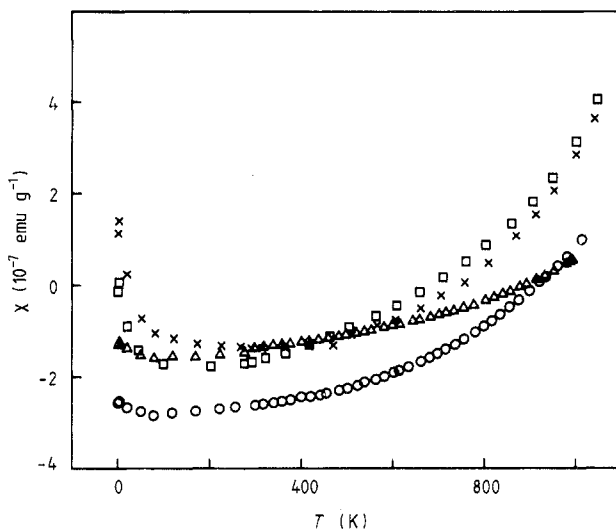
Figure 1. Susceptibility of the Al–Cu–Fe icosahedral phase at high magnetic fields (50 kOe below 300 K, 10 kOe above it) as a function of temperature, the lowest of which is 2 K. $\square$, $\times$, $Al_{65}Cu_{20}Fe_{15}$; $\triangle$, $Al_{65}Cu_{20}Fe_{14}$; $\bigcirc$, $Al_{65}Cu_{21}Fe_{14}$. The susceptibility seems to be strongly dependent on the composition of the samples.

The samples were prepared by the same method as in [5]. Figure 1 shows the susceptibility at high magnetic fields as a function of T. The absolute value of the susceptibilty is of the order of 10^{-7} emu g^{-1} [6]. It shows only a quite small increase at low temperatures (see the scale of the ordinate) in spite of the considerable concentration of Fe. The dependence of the magnetisation on the magnetic field, H, shows a slight curvature at the lowest temperature, 2 K. After subtracting the background susceptibility, extrapolation of the magnetisation between 1.5 and 5 T to $1/H \to 0$ gives a saturation value of less than 10^{-3} emu g^{-1}, which is 10^{-4} of that for the Al–Mn–Si quasicrystal [7]. These facts mean that the Al–Cu–Fe icosahedral phase has almost no magnetic moment.

The presence of little or no local magnetic moment of Fe in the Al–Cu–Fe icosahedral phase is similar to the situation found for Fe in pure Al [8]. This may be understood by employing both the concept of Friedel virtual bound states [9] and the Anderson criterion for local magnetic moment formation [10, 11], although the Anderson and Friedel theory assumes dilute alloys, and application to the present alloy should be taken only as a rough approximation. The atomic energy levels of 3s and 3p states of Al, 4s states of Cu and 3d states of Fe are -10.11, -4.86, -6.92 and -16.54 eV [12], respectively, the last of which is well below the other levels. It means that the 3d states of Fe must be located well below E_F in the s and p bands of the icosahedral phase and the 3d states may be understood as the virtual bound states, whose typical width is a few eV. The virtual bound states may have, therefore, quite a small tail at E_F, and the criterion for local magnetic moment formation by Anderson [10, 11] should not be satisfied

$$UN_{d\uparrow}(E_F) \leqslant 1 \tag{1}$$

where U is the intra-atomic Coulomb interaction of the order of 1 eV and $N_{d\uparrow}(E_F)$ is the DOS for one spin.
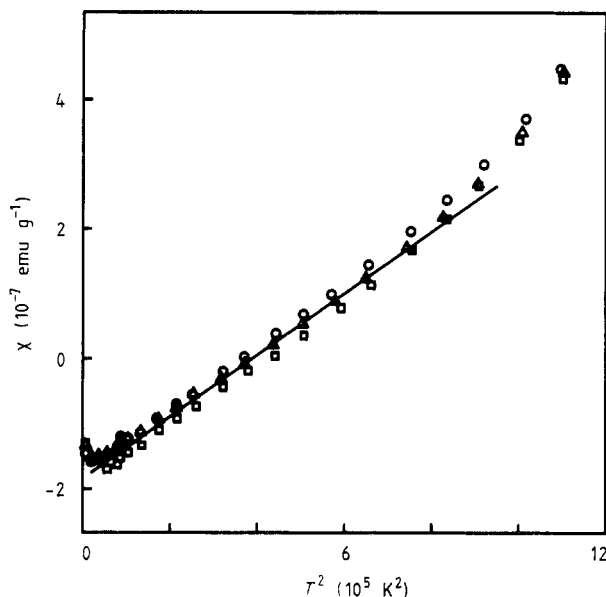
Figure 2. Susceptibility of three $Al_{65}Cu_{20}Fe_{15}$ samples as a function of the square of temperature, which shows a linear relationship below 800 K [5]. The susceptibility of the three samples with the same composition is almost the same.

Above 100 K an increase in the susceptibility χ with temperature is observed. The increase is strongly dependent on the composition of the samples (figure 1), whereas it is almost the same for the samples with the same composition, as shown in figure 2. The T^2 dependence of χ shown in figure 2 may be accounted for by the temperature dependence of Pauli paramagnetism or by the contribution from conduction electrons interacting with spin fluctuation of local magnetic moments [13]. The latter should however, be, discarded, because the icosahedral phase has almost no local magnetic moment, as mentioned above. Subtraction of the diamagnetic core contribution from the values extrapolated to 0 K (figures 1 and 2) leaves an almost zero or very small paramagnetic contribution of the order of $0–5 \times 10^{-7}$ emu g^{-1}, depending on the values of the core contribution adopted [14].

The positive gradient in the $\chi–T^2$ plot (figure 2), therefore, results in the condition that the coefficient of the T^2 term in the following expression for the temperature dependence of the Pauli paramagnetism must be positive:

$$\chi_P = 2\mu_B^2 N(E_F)[1 + \tfrac{1}{6}\pi^2 k^2 T^2\{(1/N)(d^2N/dE^2) - [(1/N)(dN/dE)]^2\}]. \tag{2}$$

The second derivative of the DOS, $d^2N(E_F)/dE^2$, must be positive, because the second term in { } is always negative. The value of $d^2N(E_F)/dE^2$ is estimated to be about 5×10^6 states Ryd^{-3}/atom or more from the experimental result, which is about several tenths of that for typical high T_c A-15 compounds [15, 16]. The positive $d^2N(E_F)/dE^2$ may originate from the s and p bands, because the 3d virtual bound state is considered to be well below E_F, as discussed above.

The structure of the DOS of the s and p bands at E_F may be inferred from the diffraction experiments as follows. The electron diffraction pattern (figure 3(a)) shows the strong spots denoted M and N, which are directed along the five-fold and the two-fold axes of
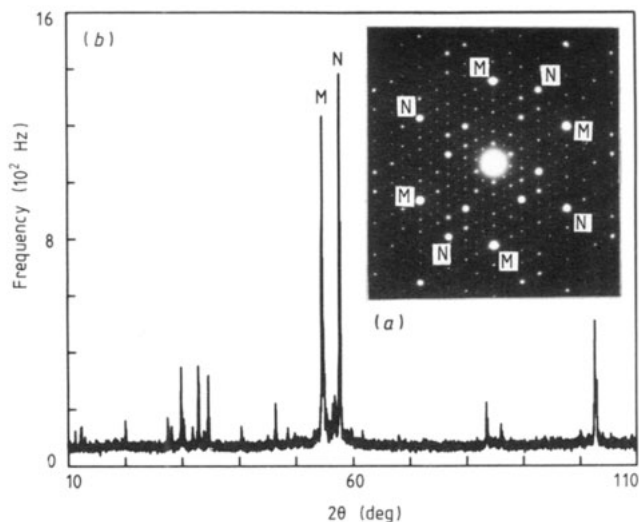
Figure 3. (*a*) Electron diffraction pattern of the $Al_{65}Cu_{20}Fe_{15}$ icosahedral phase showing strong spots along the five-fold axis (M) and the two-fold axis (N); (*b*) x-ray powder pattern showing the two strong peaks arising from the spots M and N.

the icosahedral symmetry. The spots correspond to the two strong x-ray powder peaks denoted by the same symbols in figure 3(*b*), where the intensities of the two peaks are one order of magnitude larger than the neighbouring peaks located near the Fermi square, discussed below when considerating the multiplicity of the peaks. The strong diffraction spots suggest that the matrix elements of the ion potential $\langle K_2 | V | K_1 \rangle$ are large if $(K_2 - K_1)$ coincides with the reciprocal lattice vectors determined from the diffraction experiments.

The influence of the matrix elements on the one-electron energy can be taken into account in the simplest approximation as a perturbation on the unperturbed free-electron state. Degenerate unperturbed states are most seriously affected by the perturbation, and the degeneracy is lifted. As a result, band gaps are formed, and the DOS near the band gap is enhanced. Such an idea of a 'Brillouin zone' has been proposed for the Al–Li–Cu icosahedral phase by Friedel and Dénoyer [17, 18], and recently applied to the interpretation of the small DOS obtained from the low-temperature specific-heat measurement [19]. The perturbative concept, based on the free-electron states with well defined wavenumbers, must be carefully applied from the fundamental point of view, because Bloch's theorem should not hold in the icosahedral phase owing to the lack of translational symmetry. It may, however, be possible that the plane-wave states are nearly the eigenstates of the phase at some special points of the reciprocal space, which has been shown for the lattice vibration states [20].

The planes in reciprocal space across which large band gaps are formed are easily obtained from the diffraction data [5, 21]. Figure 4(*a*) shows the perspective of the polyhedron that is formed by 12 identical pentagons and 30 identical hexagons, and the full line in figure 4(*b*) shows a section of the polyhedron crossing the origin perpendicular to a two-fold axis. The wavenumbers of the distances from the origin to the planes are $0.2371\ \text{Å}^{-1}$ and $0.2493\ \text{Å}^{-1}$, respectively. The polyhedron, therefore, closely resembles a sphere.

(a)   (b)
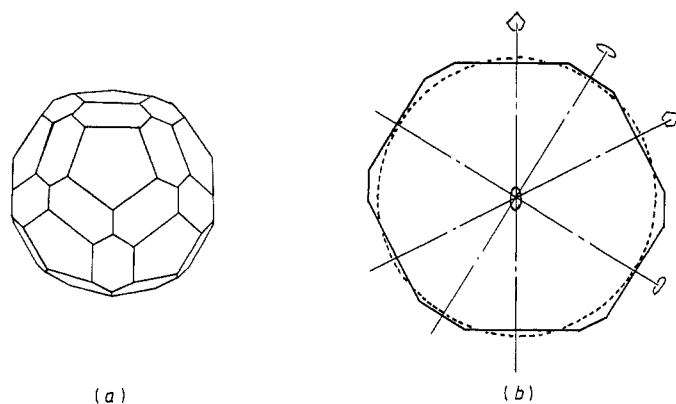
Figure 4. (a) Perspective of the polyhedron with 12 pentagons and 30 hexagons across which gaps in the energy of the electron are inferred from the strong diffraction spots shown in figure 3; (b) section of the polyhedron crossing the origin perpendicular to a two-fold axis (full line) and the Fermi sphere with radius 0.2453 Å^{-1} (broken line), which indicates a close agreement of the polyhedron and the Fermi sphere. The axes are directed in the same way as in figure 3(a).

Table 1. Mass density in unit of g cm^{-3} of the two icosahedral phases, $Al_{65}Cu_{21}Fe_{14}$ and Al_4Mn. The experimental value of $Al_{65}Cu_{21}Fe_{14}$ is obtained in the present work to an accuracy of within a few per cent by the method explained in the text. The experimental value of Al_4Mn is taken from reference [22], whose value is consistent with reference [23]. The estimated values are calculated by the use of the average atomic volumes and the atomic weights of the constituent atoms.

	Experimental	Estimated
$Al_{65}Cu_{21}Fe_{14}$	4.31	4.30
Al_4Mn	3.57–3.55	3.43

The Fermi wavenumber K_F of the unperturbed free-electron sphere is estimated by the use of the values of the s and p valence and the mass density of the sample. An Al atom has two 3s and one 3p electrons, and a Cu atom has one 4s electron. The 3d states of Fe may be considered as the virtual bound states as discussed above, and they may accommodate at most two electrons from the s and p states well above the virtual bound states. If the electron–electron interaction in the virtual bound states is taken into account, the one-electron energies of the states may be raised and the number of electrons to be accommodated may be less than two (zero at the lowest).

The mass density of the $Al_{65}Cu_{21}Fe_{14}$ sample was measured by the use of a Beckman model 930 air comparison pycnometer. It essentially measures the volume of the sample by applying air pressure of two atmospheres, avoiding an error that might originate from there being many cracks in the sample. The instrument was calibrated using a standard sample with known volume that is identical to the sample volume 1.44 cm^3 to within 7%. The mass density was determined as 4.31 g cm^{-3} to an accuracy of a few per cent by this procedure. In table 1 the value is compared with the value estimated from the average atomic volumes of Al, Cu and Fe for each pure metal. A similar comparison is also made
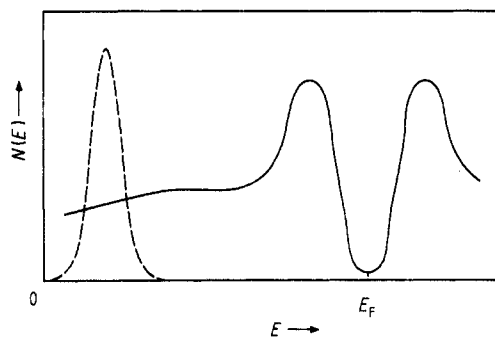
Figure 5. Schematic electronic density of states inferred from the situation shown in figure 4, which has a deep valley near E_F arising from the band gaps of the polyhedron. The broken line shows the virtual bound states.

in the table for the Al_4Mn icosahedral phase. The measured values agree well with the estimated values.

The s and p valence and the mass density give 0.2453 Å^{-1} and 0.2578 Å^{-1} for K_F for electron accommodation 2 and 0 of the virtual bound states, respectively, by the use of a relation

$$K_F = 3(3\pi^2\rho)^{1/2}/2\pi \tag{3}$$

where ρ is the electron density per unit volume. These K_F values are close to the distances from the origin to the planes across which large energy gaps are expected. The Fermi sphere with radius 0.2453 Å^{-1} is drawn by a broken line together with the polyhedron in figure 4(*b*), which shows a close agreement with the sphere. The volume ratio of the Fermi sphere to the polyhedron is 0.93 and 1.01 for the electron accommodation 2 and 0 of the virtual bound states, respectively.

The characteristic of the DOS near E_F expected from the above model is shown schematically in figure 5, which has a deep valley near E_F arising from the band gaps across the planes of the polyhedron. The T^2 dependence of χ is, therefore, considered to afford strong experimental evidence for the band gap at E_F in the icosahedral phase, which is consistent with the small DOS obtained from the specific-heat measurement [19]. The T^2 dependence was found at least below 800 K [5], which means that the width of the valley is at least of the order of 0.1 eV. The stable Al–Cu–Fe icosahedral phase, which does not crystallise even on annealing for 24 hours at 1090 K, may be stabilised by such an electronic origin [17–19] resulting from the band gaps and the enhanced DOS below E_F lowering the electronic energy, whereas the metastable icosahedral alloys [19] and the amorphous $Cu_{60}Zr_{40}$ [24], which do crystallise on annealing, have been reported not to show a small DOS at E_F.

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