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Ab-initio, Mößbauer spectroscopy, and magnetic study of the approximant $Al_{72}Ni_{9}Fe_{19}$ to a decagonal Al-Ni-Fe quasicrystal

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ABSTRACT

We report the results of *ab-initio* electronic structure and electric field gradient calculations and of X-ray diffraction, ^{57}Fe Mößbauer spectroscopy, and magnetic studies of the approximant $Al_{72}Ni_{9}Fe_{19}$ to a decagonal Al-Ni-Fe quasicrystal. The approximant crystallizes in the hexagonal space group $P6_3/mmc$ with the lattice parameters $a = 7.6989(2)$ Å and $c = 7.6724(2)$ Å. A pseudogap in the density of states, centered at ~0.30 eV above the Fermi level and with a width of ~0.35 eV, is found. Evidence for the covalent nature of the chemical bonding and good metallicity of $Al_{72}Ni_{9}Fe_{19}$ is provided. The Mößbauer spectra and a $1/T$-like dependence of the magnetic susceptibility indicate that $Al_{72}Ni_{9}Fe_{19}$ is a paramagnet down to 2.0 K. The shape of the Mößbauer spectra is accounted for by a superposition of two quadrupole doublets corresponding to Fe atoms located at two inequivalent crystallographic sites. A sudden change of the quadrupole splittings of the two doublets at ~200 K indicates a possible structural phase transition. Excellent agreement between the calculated and measured quadrupole splittings is observed. The Debye temperature of $Al_{72}Ni_{9}Fe_{19}$ is found to be 431 (3) K.

1. Introduction

Solids are formed as crystalline, quasicrystalline, or amorphous. Quasicrystals (quasicrystalline solids) possess a new type of long-range translational order, quasiperiodicity, and a noncrystallographic orientational order associated with classically forbidden fivefold, eightfold, tenfold, and twelvefold symmetry axes [1]. Discovery of new quasicrystals [2] and studies of their physical properties [3] are often helped by studying so-called approximants. An approximant to a quasicrystal is a structurally complex crystalline compound whose composition and structural units are very similar to those of the quasicrystal [4–6].

The intermetallic compound Al_5Co_2 was shown [7] to be an approximant to Al-Co-based decagonal quasicrystals. The first refinement of the Al_5Co_2 crystal structure, that was based on the analysis of the diffraction intensities obtained from Weisenberg photographs of single crystals [8], established that Al_5Co_2 crystallizes in the hexagonal space group $P6_3/mmc$ with the lattice parameters $a = 7.656(3)$ Å and $c = 7.593(2)$ Å. Other refinements that followed, of both powder and single crystal X-ray diffraction data of Al_5Co_2 [9,10], confirmed the correctness of the choice of the space group.

Electronic structure calculations predict [11–14] the presence of a minimum in the Al_5Co_2 density of states (DOS), called a pseudogap, at the Fermi energy (E_F). The existence of such a pseudogap at or in the close vicinity of E_F is a characteristic DOS feature of some decagonal and all icosahedral quasicrystals [1]. The existence of the theoretically predicted pseudogap in the DOS(E_F) of Al_5Co_2 was confirmed experimentally [12].

It was Bradley and Taylor [15] who observed for the first time that the structure of ternary Al-rich Al-Ni-Fe alloys containing Fe and Ni in certain proportions is the same as that of Al_5Co_2. Specifically, they found out that $Al_{10}NiFe_3$ ($Al_{71.4}Ni_{7.1}Fe_{21.4}$) has exactly the same type of structure as Al_5Co_2, but did not provide the lattice parameters of the hexagonal unit cell of $Al_{10}NiFe_3$. Thus, $Al_{10}NiFe_3$ can be regarded as an approximant to a decagonal Al-Ni-Fe quasicrystal. The lattice parameters $a = 7.70937(5)$ Å and $c = 7.67947(8)$ Å and atomic coordinates for an alloy of similar nominal composition $Al_{71.5}Ni_{10}Fe_{18.5}$ (empirical composition $Al_{71.4}Ni_{10.2}Fe_{19.1}$) were determined from the single crystal X-ray diffraction data [16].

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Here we report the results of *ab-initio*, X-ray diffraction, ^{57}Fe Mößbauer spectroscopy, and magnetic study of $Al_{72}Ni_9Fe_{19}$, an approximant to a decagonal Al-Ni-Fe quasicrystal.

2. Theoretical and experimental methods

Ab initio electronic structure and Mößbauer hyperfine-interaction parameter calculations have been performed within the framework of density functional theory using the full-potential linearized augmented-plane-wave plus local orbitals (FP-LAPW+lo) method as implemented in the WIEN2k package [17]. In this method, the unit cell is partitioned into two regions: a region of non-overlapping muffin-tin (MT) spheres centered at the atomic sites and an interstitial region. The wave functions in the MT regions are a linear combination of atomic radial functions times spherical harmonics, whereas in the interstitial regions they are expanded in plane waves. The basis set inside each MT sphere is split into a core and a valence subset. The core states are treated within the spherical part of the potential only and are assumed to have a spherically symmetric charge density in the MT spheres. The valence wave functions in the interstitial region were expanded in spherical harmonics up to $l = 4$, whereas in the MT region they were expanded to a maximum of $l = 12$ harmonics. For the exchange-correlation potential, the generalized gradient approximation (GGA) scheme of Perdew, Burke, and Ernzerhof [18] was used. A separation energy of −6.0 Ry between the valence and core states of individual atoms in the unit cell was chosen.

The values of 1.99, 2.31, and 2.31 a.u. were used as the MT radii for Al, Fe, and Ni, respectively. The plane-wave cut-off parameter was set to $R_{MT} \times K_{MAX} = 6.5$, where R_{MT} is the smallest MT radius in the unit cell and K_{MAX} is the maximum K vector used in the plane-wave expansion in the interstitial region. A total of 1000 k-points were used within a $10 \times 10 \times 9$ k-mesh in the irreducible wedge of the first Brillouin zone. A convergence criterion for self-consistent field calculations was chosen in such a way that the difference in energy between two successive iterations did not exceed 10^{-4} Ry. The experimental lattice parameters (a and c) and the atomic position parameters (*vide infra*) were used in the calculations.

An ingot of nominal composition $Al_{72}Ni_9Fe_{19}$ (point 1 in Fig. 1 of [19]) was prepared by inductive melting of the constituent elements in a water-cooled copper crucible under an argon atmosphere. It was then annealed at 1073 K for 550 h and then water quenched.

X-ray diffraction measurements were carried out at 298 K in Bragg-Brentano geometry on a PANalytical X'Pert scanning diffractometer using Cu $K\alpha$ radiation in the 2θ range 20–120° in steps of 0.02°. The $K\beta$ line was eliminated by using a Kevex PSi2 Peltier-cooled solid-state Si detector.

The dc magnetization was measured in the temperature range from 2.0 to 350 K and in magnetic fields up to 90 kOe using the vibrating sample magnetometer (VSM) option of the Quantum Design physical property measurement system (PPMS). The dc magnetic susceptibility was measured using PPMS in the magnetic field of 10 kOe in the temperature range of 2–390 K.

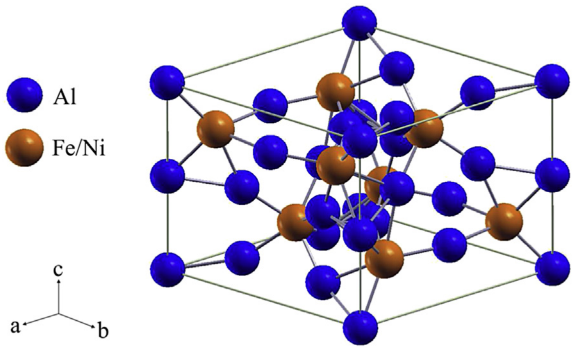

Fig. 1. The unit cell of the $Al_{72}Ni_9Fe_{19}$ compound.

The ^{57}Fe Mößbauer measurements [20] were conducted using a standard Mößbauer spectrometer operating in the sine mode and a ^{57}Co(Rh) source at room temperature. The spectrometer was calibrated with a 6.35-μm-thick α-Fe foil [21] and the spectra were folded. The Mößbauer absorber consisted of a mixture of powdered $Al_{72}Ni_9Fe_{19}$, and powdered boron nitride, which was pressed into a pellet and put into a high-purity, 8-μm-thick Al disk container to ensure a uniform temperature over the whole absorber. The Mößbauer absorber was put into a Mößbauer cryostat in which it was kept in a static exchange gas atmosphere at a pressure of ~6×10^{-3} mbar. The surface density of the Mößbauer absorber was 12.9 mg/cm^2. This corresponds to an effective thickness parameter $t_a = 2.3f_a$, where f_a is the Debye-Waller factor of the absorber. Since $t_a > 1$, the resonance line shape of the Mößbauer spectra was described using a transmission integral formula [22].

3. Results and discussion

3.1. Structural characterization

The compound studied, $Al_{72}Ni_9Fe_{19}$, analogously to the Al_5Co_2 compound, crystallizes in the hexagonal space group $P6_3/mmc$ (No. 194) [8]. The crystal structure of $Al_{72}Ni_9Fe_{19}$ is shown in Fig. 1. The rods connecting the Al, Ni, and Fe atoms (Fig. 1) describe the directional covalent bonding between these atoms (*vide infra*).

Fig. 2 displays the X-ray powder diffraction pattern of $Al_{72}Ni_9Fe_{19}$. A Rietveld refinement [23] of the X-ray powder diffraction data was carried out, yielding the lattice parameters $a = 7.6989(2)$ Å and $c = 7.6724(2)$ Å, and the atomic positional parameters that are listed in Table 1. The values of these lattice and atomic positional parameters are very close to the corresponding values for the $Al_{71.5}Ni_{10}Fe_{18.5}$ alloy [16]. No second phase/phases could be detected in the X-ray diffraction pattern of $Al_{72}Ni_9Fe_{19}$ (Fig. 2).

3.2. Ab-initio calculations

3.2.1. Electronic structure

The calculated total and atom-resolved density of states (DOS) of $Al_{72}Ni_9Fe_{19}$ is shown in Fig. 3. One observes that the total DOS outside the energy region from about −4 to 1 eV with respect to the

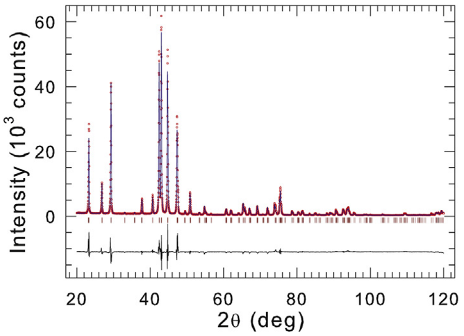

Fig. 2. Powder X-ray diffraction pattern of $Al_{72}Ni_9Fe_{19}$ at 298 K. The experimental data are denoted by open circles, while the line through the circles represents the results of the Rietveld refinement. The row of vertical bars shows the Bragg peak positions for the $P6_3/mmc$ space group. The lower solid line represents the difference curve between experimental and calculated patterns.