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Physical properties of the V-$Al_5Cu_6Mg_2$ complex intermetallic phase

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ABSTRACT

The cubic V-$Al_5Cu_6Mg_2$ phase with 39 atoms in the unit cell is an intermetallic phase with intermediate structural complexity between the simple Laves phase and the complex Bergman phase. Using ^{27}Al NMR spectroscopy, we have determined the electric-field-gradient tensors at the positions of three crystallographically nonequivalent Al sites in the unit cell and confirmed the local site symmetries of these sites, as predicted by the Samson structural model of the V-phase from 1949. The influence of structural complexity on the physical properties of a solid was studied by determining bulk electrical and thermal properties (electrical resistivity, thermoelectric power, Hall coefficient, thermal conductivity and specific heat) and local electronic properties of the V-$Al_5Cu_6Mg_2$ monocrystal by studying the ^{27}Al NMR Knight shift and the spin-lattice relaxation rate. The experiments reveal that free-electron picture is good approximation to the V-$Al_5Cu_6Mg_2$ electronic structure, despite the structural complexity of the lattice. The positive thermopower and Hall coefficient reveal that V-$Al_5Cu_6Mg_2$ is a hole-type electrical conductor. Electrical resistivity shows linear temperature dependence with a positive temperature coefficient, typical of regular metals and alloys. The relatively large $T \rightarrow 0$ residual resistivity and the low thermal conductivity suggest the presence of quenched structural disorder, very likely intrinsic to the V-$Al_5Cu_6Mg_2$ structure. We did not find any experimental evidence of a pseudogap close to the Fermi energy in the electronic density of states that could contribute to the electronic stabilization of the structure.

1. Introduction

"Complex metallic alloys" (CMAs) denote intermetallic phases with giant unit cells comprising some hundred up to many thousands of atoms [1]. The giant unit cells with lattice parameters of several nanometers provide translational periodicity of the CMA crystalline lattice on the scale of many interatomic distances, whereas on the atomic scale, the atoms are arranged in clusters with polyhedral order, where icosahedrally coordinated environments play a prominent role. The structures of CMAs show duality; on the scale of several nanometers, CMAs are periodic crystals, whereas on the atomic scale many of them resemble quasicrystals (QCs) [2]. The high structural complexity of CMAs together with the two competing physical length scales—one defined by the unit-cell parameters and the other by the cluster substructure—may have a significant impact on the physical properties of these materials, such as the electronic structure and lattice dynamics.

Examples of CMAs are the cubic $NaCd_2$ with 1152 atoms per unit cell (u.c.) [3,4], the cubic β-Al_3Mg_2 (1168 atoms/u.c.) [5–7], the heavy-fermion compound $YbCu_{4.5}$ (7448 atoms/u.c.) [8], and the *cF*(23, 256-*x*)-$Al_{55.4}Cu_{5.4}Ta_{39.1}$ phase of unprecedented complexity, comprising more than 23,000 atoms in the unit cell [9]. These giant unit cells contrast with elementary metals and simple intermetallics whose unit cells comprise from a few up to a few tens of atoms only, raising the question why nature sometimes chooses structural complexity instead of simplicity.

Recently, we succeeded to grow centimeter-size monocrystals of the V-phase $Al_5Cu_6Mg_2$ (V-$Al_5Cu_6Mg_2$). The structure of this CMA has been reported by Samson in 1949 [10], but we could not find any other literature report on this compound, neither regarding validation of the structural model nor on its physical and chemical properties. The cubic V-$Al_5Cu_6Mg_2$ phase with 39 atoms/u.c. is supposed structurally isomorphous to the Mg_2Zn_{11} phase [11,12], which is considered as an intermediate step in the increasing structural complexity within the series of (Al-)Mg-Zn compounds between the simple Laves-phase $MgZn_2$ (12 atoms/u.c.) and the

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complex Bergman phase $Mg_{32}(Al,Zn)_{49}$ (162 atoms/u.c.) [13]. The basic building block of the latter is the 105-atom Bergman icosahedral cluster, found also in icosahedral Al–Mg–Zn QCs [14].

In this paper, we first present a nuclear magnetic resonance (NMR) determination of the ^{27}Al electric field gradient (EFG) tensors at the three crystallographically nonequivalent Al sites in the unit cell of the V-$Al_5Cu_6Mg_2$ phase. Since the symmetry of the tensors equals the symmetry of local chemical environments around the ^{27}Al resonant nuclei, we are able to test specific details (site symmetry of the Al crystallographic sites) of the Samson structural model [10] on a local scale of atomic clusters. Next we study the electronic structure of the V-$Al_5Cu_6Mg_2$ compound, by determining the electronic density of states (DOS) at the Fermi energy ε_F from the ^{27}Al NMR Knight shift, the spin-lattice relaxation rate and the low-temperature specific heat. We also report the electrical and thermal transport properties of the V-$Al_5Cu_6Mg_2$ phase and discuss the possible existence of a pseudogap in the electronic DOS at ε_F.

2. Structural considerations and sample description

The V-$Al_5Cu_6Mg_2$ phase is cubic with space group $Pm3$ (No. 200), the lattice constant $a = 8.3$ Å and 39 atoms in the unit cell [10]. It is isostructural to the Mg_2Zn_{11} phase [11,12] and is also a part of a series of phases with increasing complexity in the Al–Cu–Mg system with λ_3-$Mg(Al_xCu_{1-x})_2$ isostructural to the $MgZn_2$ and $Mg_{32}(Al_xCu_{1-x})_{49}$ isostructural to the Bergman phase [15]. The unit cell contains three Al, two Cu and one Mg crystallographic site. The structure can be viewed either as a cubic packing of Pauling triacontahedra linked by Cu octahedra (Fig. 1a), or as an embedding of icosahedra in an fcc-structure matrix (Fig. 1b), or even as a network of distorted and modified overlapping Tsai-type clusters with octahedra replacing tetrahedra in the prototype binary Yb–Cd structure near the 1:6 Cd-rich composition [16,12]. Fig. 1c shows constituent shells of the Pauling triacontahedron, containing an inner Cu icosahedron with an Al atom in the center, followed by a distorted dodecahedron of Al and Mg atoms, and an outer Al icosahedron. The connecting Cu octahedron is shown as well. In Fig. 1d, the constituent shells of the Tsai-type cluster are shown, with an inner Cu octahedron, followed by a strongly distorted Al dodecahedron, and an outer Mg icosahedron. The connecting Cu icosahedron is shown as well.

It is worth mentioning that in the Samson model of the V-$Al_5Cu_6Mg_2$ phase [10], all six crystallographic sites in the unit cell are fully occupied. This is also the case for the isomorphic Mg_2Zn_{11}, considering the Samson model of that phase from 1949 [11]. However, the recently refined Mg_2Zn_{11} structural model [12] has reported that the central position of the inner Zn icosahedron (occupied by a Zn atom) inside the Pauling triacontahedron is not fully occupied, but fractionally by 72%. In the V-$Al_5Cu_6Mg_2$ unit cell, this position corresponds to the Al3 site (Wyckoff position 1*b*) in the center of the inner Cu icosahedron. Reinvestigation of the V-$Al_5Cu_6Mg_2$ structure is needed to find out whether fractional occupation applies to the Al3 site as well.

The V-$Al_5Cu_6Mg_2$ sample used in our study was an oriented monocrystal of dimensions $6.2 \times 2.2 \times 1.2$ mm^3, with its long axis along the [100] crystallographic direction. It has been grown by the Bridgman method. Crystal growth procedure will be a subject of a separate paper [17]. Structural characterization by XRD, SEM and TEM techniques has shown that the sample was single-phase. Good structural quality at the local level of atomic clusters was also confirmed by our NMR experiments, to be presented next.

3. NMR determination of the ^{27}Al EFG tensors and the Knight shift

In NMR spectroscopy, the Zeeman energy levels of quadrupolar resonant nuclei such as ^{27}Al in an external magnetic field are

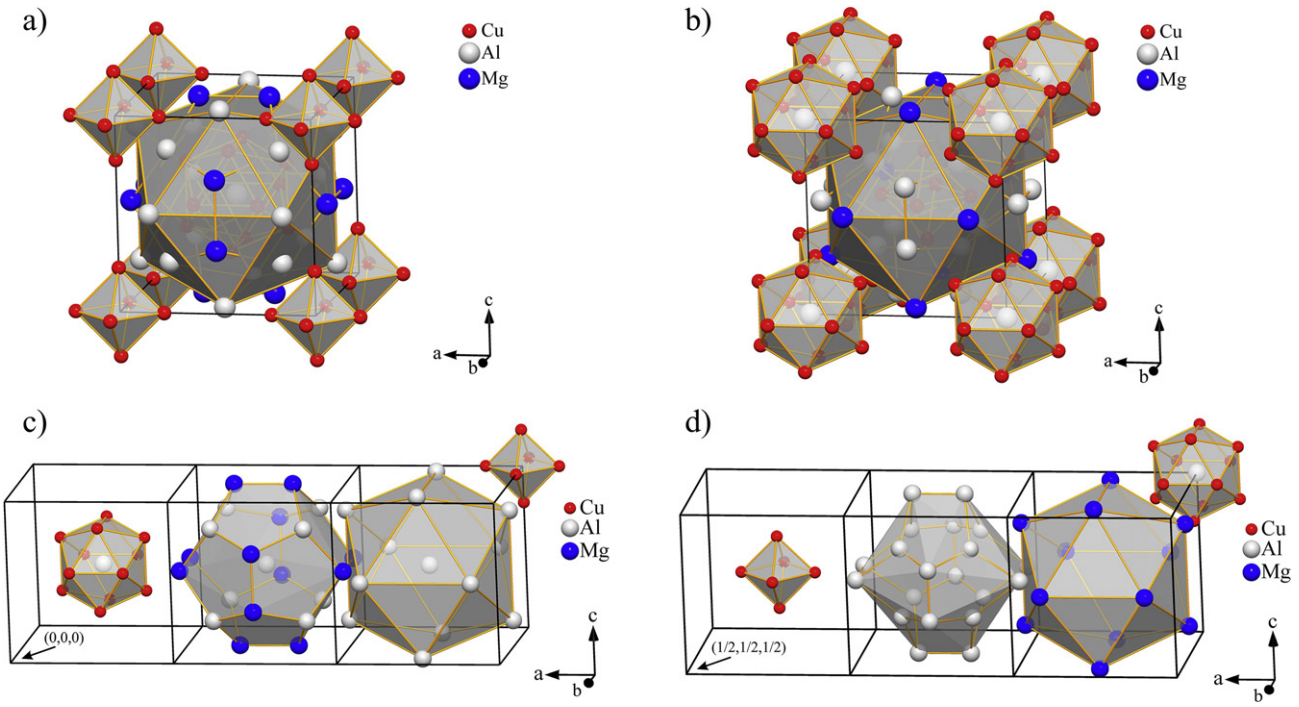

Fig. 1. (Color online) Structure of the V-$Al_5Cu_6Mg_2$ phase according to the Samson model [10]. The structure can be viewed either as (a) a cubic packing of Pauling triacontahedra linked by Cu octahedra, or (b) as an embedding of icosahedra in an fcc-structure matrix. The two representations are equivalent; one can be derived from the other by a shift for (0.5, 0.5, 0.5). Panel (c) shows constituent shells of the Pauling triacontahedron, containing an inner Cu icosahedron with an Al atom in the center, followed by a distorted dodecahedron of Al and Mg atoms, and an outer Al icosahedron. The connecting Cu octahedron is shown as well. In panel (d), the constituent shells of the Tsai-type cluster are shown, with an inner Cu octahedron, followed by a strongly distorted Al dodecahedron, and an outer Mg icosahedron. The connecting Cu icosahedron is shown as well.