

Electrical resistivity of one-dimensional quasiperiodic η^8 -Cu₅Sn₄

M. Rodmar and M. Ahlgren

Solid State Physics, Kungliga Tekniska Högskolan, SE 100 44 Stockholm, Sweden

S. Lidin

Inorganic Chemistry, Arrhenius Laboratoriet, Stockholms Universitet, SE 106 91 Stockholm, Sweden

Ö. Rapp

Solid State Physics, Kungliga Tekniska Högskolan, SE 100 44 Stockholm, Sweden

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The electrical resistivity, ρ , of one-dimensional quasiperiodic η^8 -Cu₅Sn₄ has been studied, and compared with crystalline Cu₆Sn₅ of identical basic structure (B8) and closely related atomic structure. ρ was measured between 1.5 and 300 K on needle-shaped crystals with their axes along the base lattice c direction, corresponding to the quasiperiodic direction in η^8 -Cu₅Sn₄. ρ (4 K) was found to be nine times larger in η^8 -Cu₅Sn₄ compared to Cu₆Sn₅, and the residual ratio R [$=\rho(4\text{ K})/\rho(300\text{ K}) < 1$] was larger by a factor of 3. The similar structures and these large differences in transport properties indicate that the effect of quasiperiodic ordering has been observed in the resistivity of a one-dimensional metal. [S0163-1829(99)04930-9]

I. INTRODUCTION

The anomalous electronic transport properties of quasicrystals are most strikingly displayed in three-dimensional (3D) crystals, and consequently these materials have attracted the strongest interest by experimentalists. 2D systems, such as decagonal quasicrystals with periodically stacked quasiperiodic planes, have also been frequently studied. These results are less surprising however, since properties in the quasiperiodic direction usually on a reduced scale reflect those of three-dimensional quasicrystals, while transport properties in the periodic direction are frequently similar to ordinary metallic alloys.¹ In contrast, transport measurements in one-dimensional quasiperiodic crystals do not seem to have been reported before.

In two or three dimensions the distinction between a quasicrystal and an incommensurably modulated phase is straightforward. The quasicrystal exhibits noncrystallographic symmetry. Further, while incommensurably modulated phases may be assigned a mean lattice, this is not possible for the quasicrystals. In one dimension there are no crystallographically forbidden symmetries and any lattice may be assigned a mean lattice, and thus the distinction between an incommensurably modulated phase and a quasicrystalline structure becomes diffuse. We will use the notation quasiperiodic throughout to avoid any confusion.

One-dimensional quasiperiodic crystals are conceptually simpler than 2D and 3D quasicrystals, and may serve the purpose to give perspicuous models,² including calculations of transport properties.^{2,3} Clearly experimental results in this area may therefore be beneficial for joint theoretical and experimental efforts to understand electronic transport in quasicrystals.

In the present paper we report on results for the electrical resistivity, ρ , and its temperature dependence on two intermetallic compounds of Cu-Sn close to 45 at. % Sn: Cu₆Sn₅ and η^8 -Cu₅Sn₄. These structures are both related to the hex-

agonal NiAs-type structure (B8), and are quite similar. However, Cu₆Sn₅ is periodic in all directions with a monoclinic cell,⁴ while η^8 -Cu₅Sn₄ has a quasiperiodic atomic arrangement in one direction.⁵ The residual resistance ratio, $R = \rho(4\text{ K})/\rho(300\text{ K})$, was found to be 0.13 for the periodic sample and 0.37 for the quasiperiodic sample. R is thus < 1 in both cases. ρ and R are small on the scale of properties usually studied in quasicrystals. However, when going from a periodic to a quasiperiodic structure, the changes observed in both quantities are in the direction expected for quasiperiodic ordering, with an increase in the low-temperature resistivity by a factor of 9 and in R by a factor of 3.

II. STRUCTURE OF Cu₆Sn₅ AND η^8 -Cu₅Sn₄

The system Cu-Sn contains a region around 45% Sn with several phases of a basic NiAs (B8)-type structure and different superstructure ordering. At temperatures below 459 K the stable phase has the ideal composition Cu₆Sn₅. This compound is a commensurate modulation ($q = \frac{1}{5} \frac{1}{5} \frac{1}{5}$) of the basic NiAs structure.⁴ It crystallizes in the monoclinic space group $C2/c$ with the cell parameters $a = 11.022$, $b = 7.282$, $c = 9.827$ (Å) and $\beta = 98.84^\circ$. Because of mimetic twinning, the exterior shape of the crystals is perfectly hexagonal, and the physical properties of a macroscopic sample are expected to exhibit hexagonal symmetry as well. At temperatures between 459 K and the melting point there exist a number of more or less well-ordered phases. Because of the negligible heat of transformation between these it is difficult to determine their respective stability intervals, but at 600 K the stable phase is η^8 -Cu₅Sn₄. This is an incommensurate modulation ($q \approx \frac{3}{8} \frac{3}{8} \frac{1}{2}$), which can be approximated by a monoclinic superstructure crystallizing in $P21/c$ with the cell axes 9.83, 9.83, 7.27 (Å) and $\beta = 62.5^\circ$. At higher temperatures, other modulations take over, and close to the melting

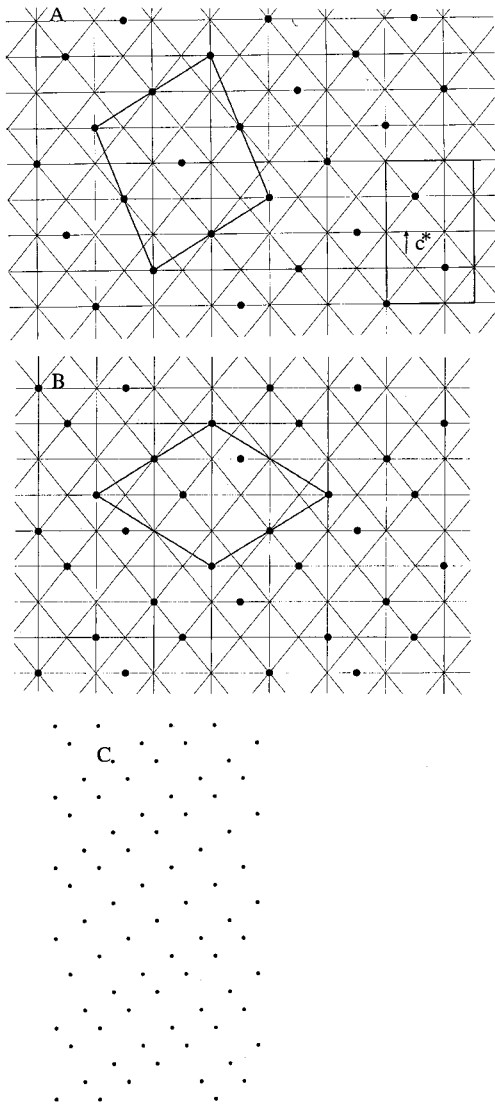


FIG. 1. (a) The structure of Cu_6Sn_5 . The basic NiAs structure consists of hexagonally close-packed tin atoms, and copper occupying all octahedral interstices. The light hatching shows the array of Sn octahedra from the side. Black circles indicate the positions of the extra Cu atoms causing the superstructure. The unit cell is shown to the left. The largest feature common to Cu_6Sn_5 and Cu_5Sn_4 is indicated by the box to the right together with the reciprocal c^* direction of the hexagonal base lattice. The direction of the resistivity measurements is $\parallel c^*$. (b) A periodic approximant of $\eta^8\text{-Cu}_5\text{Sn}_4$ with a unit cell indicated. The underlying NiAs structure is indicated as in (a). Note the similarity with Cu_6Sn_5 . (c) The true structure of $\eta^8\text{-Cu}_5\text{Sn}_4$ is most likely an incommensurately ordered intergrowth between the ordered structure and elements from Cu_6Sn_5 . A set of positions of the extra Cu atoms of one such arrangement is proposed. Current is along the vertical direction $\parallel c^*$ in (a).

point at 688 K superstructure ordering is discernible as diffuse scattering in electron diffraction only.

Simplified pictures of the atomic ordering of the two structures are shown in Fig. 1. Cu_6Sn_5 and $\eta^8\text{-Cu}_5\text{Sn}_4$ are remarkably similar with identical basic structures. Due to the sparse arrangement of extra Cu atoms the deformations around these atoms are also comparable. The smallest unique distance distinguishing the two structures is about 3.5 \AA . To

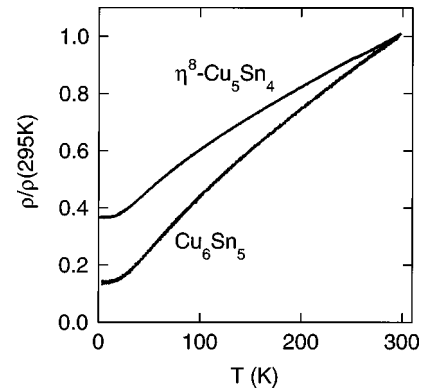


FIG. 2. The temperature dependence of the normalized resistivity of $\eta^8\text{-Cu}_5\text{Sn}_4$ and Cu_6Sn_5 .

appreciate the magnitude of this distance and further emphasize the similarity between the structures, it can be mentioned that the 47 smallest atomic distances in Cu_6Sn_5 have been listed previously, all of them below 2.9 \AA .⁴ The largest common feature between the two structures is indicated in Fig. 1(a), and is roughly $6 \times 10 \text{ \AA}^2$.

III. SAMPLE PREPARATION AND MEASUREMENTS

Single crystals of the two phases were grown from a tin-rich melt (90% Sn) which was first homogenized at 1073 K for 24 h. The temperature was then lowered to 623 K and kept there for 72 h. The high-temperature phase was subsequently annealed at 573 K for 240 h and the low-temperature specimen was treated at 453 K for 480 h. The samples were then quenched in water and the excess Sn was removed by leaching in 6 M HCl.

The samples produced by this technique were in the form of hexagonal prisms of lengths 1–2 mm and thickness about 0.1 mm. Resistance measurements along the axis of the samples were performed by an ordinary four-pole technique. The contacts were made with silver paint, and no heat treatment. Due to the small sample size it was not possible to make measurements in the other crystal directions. Measurements were performed in an ordinary ^4He cryostat between 1.5 and 300 K.

IV. RESULTS AND DISCUSSION

The electrical resistivity is shown in Fig. 2. Both samples show a typical metallic behavior in the temperature dependence; ρ decreases with decreasing temperature and saturates at a constant value below about 20 K. However, clear differences were observed between the periodic and quasiperiodic samples. The measured values of ρ at 295 K were 15 and $49 \mu\Omega \text{ cm}$ respectively, with a significantly larger value for the quasiperiodic direction, also when taking into account the large error in the resistivity measurements of $\approx 25\%$, due to the small sample dimensions. The R values show a corresponding change from 0.14 for the periodic sample to 0.37 for the quasiperiodic one.

These results may be compared with those observed in amorphous Cu-Sn. Quench-condensed amorphous $\text{Cu}_x\text{Sn}_{1-x}$ films are stable at low temperatures over a concentration range from $x=0.1$ to 0.8.⁶ In the region between $x=0.5$ to

0.6, the resistivity at 10 K is about $80 \mu\Omega \text{ cm}$ and increases with increasing temperature up to a maximum value at about 40 K, followed by a region of weakly decreasing resistivity up to the highest measurement temperature around 80 K.⁶ The low-temperature resistivity for $\eta^8\text{-Cu}_5\text{Sn}_4$ is roughly four times smaller, and the temperature dependence in Fig. 2 is clearly different.

Furthermore, the amorphous samples were superconducting below a critical temperature T_c , which decreased linearly with increasing x , and reached below 2 K for $x=0.6$.⁷ Since copper is almost insoluble in tin, tempered polycrystalline thin films show a T_c reflecting that of Sn.⁸ In contrast, for the samples in Fig. 2 there is no trace of a superconducting transition at lower temperatures in any of the two samples from measurements down to 1.5 K, with a temperature-independent $\rho(T)$ below 4 K within the measurement accuracy. Already remnants (well below 1 at. %) of Sn or an amorphous phase could be expected to affect the resistivity in the direction of a superconducting transition. Our results confirm phase-pure samples, and illustrate the strongly modified properties obtained when ordering periodically or quasiperiodically the amorphous phase.

To estimate the electronic mean free path l , we need information about the carrier density and Fermi velocity, which are not known for Cu_6Sn_5 and $\eta^8\text{-Cu}_5\text{Sn}_4$. For amorphous $\text{Cu}_{55}\text{Sn}_{45}$ a free electron estimate of l is likely appropriate. From $l = (\hbar/e^2)(3\pi^2)^{1/3}/(n^{2/3}\rho)$, with ρ from Ref. 6, and the carrier concentration n from Hall-effect measurements,⁸ we find l to be about 6 Å, which is a fairly typical value for amorphous metals. Since ρ of $\eta^8\text{-Cu}_5\text{Sn}_4$ and Cu_6Sn_5 is smaller or much smaller, and n is likely to be similar or smaller, this estimate is a lower bound for both compounds.

The similar structures of Cu_6Sn_5 and $\eta^8\text{-Cu}_5\text{Sn}_4$ imply that the surroundings of each atom are identical in the two structures out to at least the second coordination shell, and in some directions even further out. Electronic band-structure properties are expected to be similar as well. If we ascribe the different electrical properties to different mean-free paths in the two structures, then l can be roughly estimated to be of the order of the length scale on which the structures of Cu_6Sn_5 and $\eta^8\text{-Cu}_5\text{Sn}_4$ differ appreciably. Taking this distance to be the maximal common length along the measurement direction, we find l of $\eta^8\text{-Cu}_5\text{Sn}_4$ to be larger than about 10 Å.

The differences in resistive properties between Cu_6Sn_5 and $\eta^8\text{-Cu}_5\text{Sn}_4$ are prominent. This is likely mainly due to the different structures even if it cannot be excluded that there are compositional fluctuations also contributing to these differences, which could be due, e.g., to accumulation or precipitation at pseudograin boundaries of nonsuperconducting microcrystallites or an amorphous phase. One must

inquire what are the reasons for these differences. Quantum interference effects (QIE) might be one possibility. The observed changes in the magnitude and temperature dependence of ρ are both in the direction expected from QIE when going from the periodic to the quasiperiodic structure. QIE are well established in quasiperiodic structures already at moderately larger low-temperature resistivities, e.g., in $\text{Mg}_{32}(\text{AlZn})_{49}$ -type icosahedral samples,⁹ where $\rho(4 \text{ K})$ is larger only by a factor of 3 as compared to $\eta^8\text{-Cu}_5\text{Sn}_4$. QIE in $\text{Mg}_{32}(\text{AlZn})_{49}$ are quite small. An upper limit is given by the variation of $\rho(T)$ between room temperature and helium temperature, which is a few percent. In lower dimensions QIE are expected to be larger at comparable resistivities. Nevertheless this interpretation remains speculative and a factor of 9 difference in $\rho(4 \text{ K})$ may be too large.

It is also interesting to note that in approximants to icosahedral Mg-Ga-Al-Zn the main features of the resistivity of the icosahedral phase, including a negative $d\rho/dT$, were reproduced only in a 2/1 cubic approximant with a lattice parameter of 23 Å, while in a 1/1 cubic approximant of lattice parameter about 14 Å, $d\rho/dT$ was positive.¹⁰ In spite of the remarkable structural similarities between Cu_6Sn_5 and $\eta^8\text{-Cu}_5\text{Sn}_4$ we must thus ask if our building blocks are not rather too small for investigating the full changes introduced by quasicrystallinity.

Magnetoresistance measurements could be a clarifying method to determine if there are contributions from QIE, strongly restricting the numerical flexibility of any theory trying to account for the observed $\rho(T)$. Unfortunately the low-temperature ρ of below about $20 \mu\Omega \text{ cm}$ appears to make such measurements unrealistic. From an extrapolation of collected data for the measured magnetoresistance of crystalline, and amorphous alloys, quasicrystals, and approximants,¹ the maximum magnetoresistance for Cu_5Sn_4 could be expected to be of order 10 ppm, which is rather too small for a reliable analysis.

In conclusion, the electrical resistivity and its temperature dependence have been measured for the first time on a one-dimensional quasiperiodic crystal, $\eta^8\text{-Cu}_5\text{Sn}_4$. Compared to Cu_6Sn_5 , a nine-fold increase of the low-temperature resistivity was observed in $\eta^8\text{-Cu}_5\text{Sn}_4$, as well as a considerably weaker temperature dependence. The similar atomic structures of these compounds suggests that these differences are mainly due to the quasiperiodic ordering.

ACKNOWLEDGMENTS

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