

LOCAL VERSUS BULK PROPERTIES OF CeAg_2Sn_2

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Results of electrical resistivity and ^{119}Sn Mössbauer effect measurements for two samples of CeAg_2Sn_2 compound are presented. A sharp drop in resistance of an annealed sample at 3.5 K might have suggested a superconducting transition while for the as-melted specimen only a modest change in ρ vs. T slope is observed at this temperature. Resonance γ -absorption reveals differences and similarities on a microscopic scale between the two samples. The occurrence of certain regions of a long-range magnetic ordering within the CeAg_2Sn_2 phase is unambiguously demonstrated by the presence of hyperfine splitting. Temperature variation of the hyperfine field follows a molecular field spin- $\frac{1}{2}$ function.

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1. Introduction

The intriguing variety of low-temperature physical properties of cerium containing intermetallics has bound much of research effort in the last two decades (e.g. [1]). Undoubtedly, in many instances the anomalous behaviour of these phases emerges from the correlations that occur between cerium $4f$ -electron and the conduction band electrons. Another important factor which strongly influences their characteristics is a coupling of a $4f$ -shell to the crystal field [2]. As all these interactions greatly depend on the structure, a systematic and comparative study of compounds within certain classes is a worthwhile job. $\text{RE}_2\text{T}_2\text{X}_2$ phases (RE — rare earth or actinide element, T — d -transition metal and X — group IIIA through VIA p -element) constitute a widely studied family of compounds with (generally) tetragonal structure (e.g. [3]). A history of a well-known, and probably most intensely studied member of this group, viz. CeCu_2Si_2 shows clearly a sensitivity of properties on details of crystallographic order. Hereafter, the electrical resistance and ^{119}Sn Mössbauer effect measurements for two differently treated samples of CeAg_2Sn_2 are presented. Preliminary resistivity results for one of them (annealed) might have suggested the occurrence of a superconducting transition at 3.5 K [4]. Magnetic susceptibility measured in an applied field of 450 Oe in the temperature range between 8 K and 250 K bears no indication of a magnetic ordering and obeys the Curie-Weiss law yielding the effective magnetic moment of $1.82\mu_B$ [5]. That is distinctly below the value of $2.54\mu_B$ which is expected for

Ce^{3+} ($4f^1$) ion. There are other cerium containing members of a subgroup of the ternary tetragonal compounds ($\text{RE}\text{T}_2\text{X}_2$) with tin as the X-constituent which have recently attracted much interest as they often show a competition between magnetic and Kondo's interactions as well as pronounced crystal field effects [6, 7]. Among them CeNi_2Sn_2 was the most extensively studied system [8, 4]. Considerable, quantitative differences in properties (resistivity, magnetic susceptibility) between annealed and unannealed samples of it were found and ascribed to lattice distortion induced by the thermal treatment [9].

2. Experimental details and results

Samples were synthesized by the arc-melting process in an inert-gas atmosphere of argon. Practically, there were no losses in weight of the pellets. Subsequently, one of them was subjected to a heat treatment at 800°C for 6 days (referred to hereafter as sample I). Sample II remained unannealed. The X-ray diffraction patterns of both samples are very much alike and can be indexed according to the primitive tetragonal $P4/nmm$ structure of a CaBe_2Ge_2 -type. Sample I, however, clearly contained some admixture of a non-identified phase as well as traces of a tin dioxide. In fact, the Mössbauer spectra of the annealed sample I show two additional (almost) single lines which are not present in the unannealed sample II (Fig. 1). The one of isomer shifts with respect to the barium stannate source equal

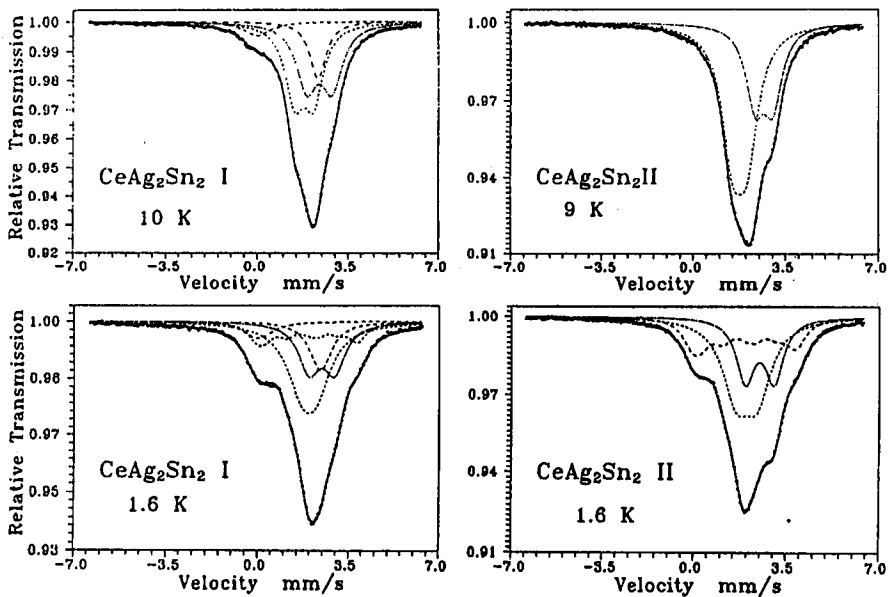


Fig. 1. ^{119}Sn Mössbauer spectra of samples I and II of CeAg_2Sn_2 at temperatures above and below the magnetic transition.

to (within error limits) zero may be unambiguously attributed to the tetravalent tin in SnO_2 . The other spectral line situated at about 2.46(2) mm/s marks another unwanted fraction. The "white" metallic β -tin cannot be ruled out. The presence of extra tin containing phases, however in small amounts, implies the deficiency of this element in the main structure of sample I causing local distortions and defects. This fact explains the slight differences in parameters of the two doublets forming the spectra of $CeAg_2Sn_2$ compound in each of studied samples whereas, generally, the respectiveness of the spectral features can be easily found (Fig. 1). The two doublets result from the electric field gradients acting at the two crystallographically nonequivalent sites on ^{119}Sn nuclei [4].

The electric resistance measurements were performed in the temperature range from 1.5 K to 300 K with a conventional four-contact method. In general, the resistivity of both samples over the temperature range 1.5–300 K possesses a metal-like form and smooth deviations from linear behaviour may tentatively be ascribed to the crystal field effects. Surprisingly enough, the unannealed sample II shows weaker temperature dependence of the resistivity which might have been expected in the case of larger crystallographic disorder, and this contradicts the above invoked conclusions. The differences between the bulk electrical properties at low temperatures are pronounced (Fig. 2a). The annealed sample I experience

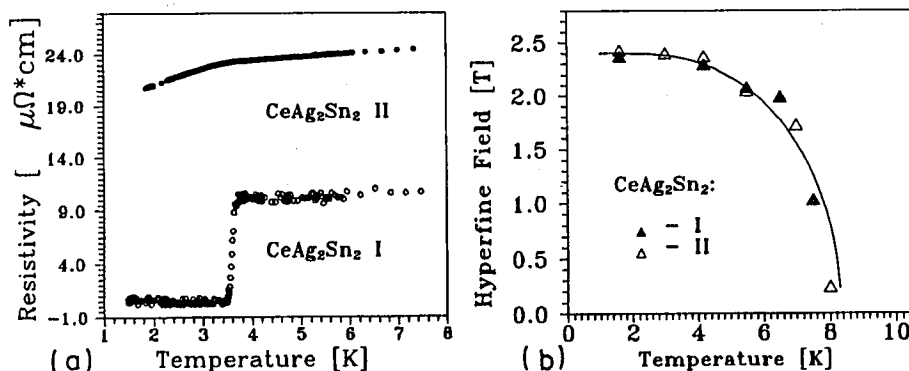


Fig. 2. (a) Temperature dependent resistivity of unannealed (I) and annealed (II) $CeAg_2Sn_2$ samples, (b) ^{119}Sn hyperfine field vs. temperature plot for the most split component of the Mössbauer spectrum (both samples as indicated in the figure).

a very sharp drop of the resistivity at 3.5(1) K while a feature being observed for sample II at the same temperature may be characterized as a modest change in the slope of temperature dependence.

The Mössbauer effect supplies a basic finding which is very puzzling. It comprises in an evident fact, common for both specimens, that a magnetic order which sets on below 8 K involves only a part of a whole volume of a given sample. This is evidenced by the appearance of a third, magnetically split component (Fig. 1) in the spectra while their substantial part hardly changes the shape. Except for their relative intensities the hyperfine patterns are identical in both

samples, and a temperature variation of the transferred hyperfine field at the tin nuclei is sample-independent (Fig. 2b). It was not possible to unambiguously decide on cost of which of the two doublets constituting the CeAg_2Sn_2 spectrum this magnetically split component is formed. It means that tin nuclei at the two crystallographically distinct sites of the ordered CeAg_2Sn_2 structure experience equal (within resolution of the method) hyperfine field when they happen to be in a magnetically ordered vicinity. Temperature dependence of the hyperfine field at the tin nuclear sites can reasonably be described as proportional to spin- $\frac{1}{2}$ molecular field magnetization (solid line in Fig. 2b). Still more astonishing statement concerns transition temperature. This quantity as derived from the temperature behaviour of the hyperfine field amounts to about 8 K (8.2(2) K) and does not correspond to the value that may be inferred from the resistivity measurements.

3. Discussion and conclusions

The microscopic characterization of the samples with ^{119}Sn Mössbauer spectroscopy proves that both specimens of nominal stoichiometry consist in the main body of the same phase (cf. Fig. 1). It is strongly supported by the finding that the strange behaviour, like a formation of the magnetically ordered regions and the temperature variation of their magnetization is identical in both samples. The T -dependence of the latter quantity is inferred from the hyperfine field acting at the tin nuclei. The field is *transferred* from cerium ions via the conduction band polarization (mainly) and in the magnetically ordered state reflects the geometry of the arrangement of the spins surrounding a given tin atom. The presence of a single hyperfine split component indicates relatively simple magnetic structure which establishes in certain regions of both samples. Ferromagnetic order with an easy axis at about 70(5) degrees to the tetragonal c -axis conforms with the present γ -absorption data. Nevertheless, a spectrum like that (i.e. with one hyperfine split component and the other two hardly affected) may arise from a more complex, antiferromagnetic spin system. It is thus not sure if the magnetic order does not extend over the whole volume of the sample. But then there still remains an open question of the difference in critical temperatures observed with bulk and local methods. The concept of the coexisting magnetically ordered and paramagnetic regions in CeAg_2Sn_2 samples seems more probable in view of experimental data. The net reduction of the cerium magnetic moment as observed in the susceptibility measurements (see [1]) may be understood as the average value. In some regions of the sample the cerium atoms preserve their one-electron occupation of the $4f$ shell and the respective magnetic moments thus favouring magnetic ordering, while in other regions (which remain paramagnetic) cerium moment is more strongly decreased. Cerium valency is determined by the local symmetry and thus crystallographic disorder may have the effect hereabout discussed. If Sn and Ag atoms exchange their places it may *locally* lead to the body centered tetragonal structure (of type ThCr_2Si_2) rather than the primitive tetragonal $P4/nmm$ structure of a CaBe_2Ge_2 -type, both having nearly equal lattice constants. This situation is not rare in this class of compounds.

Having in view the described facts it may be concluded that the low-temperature properties of $CeAg_2Sn_2$ certainly classify this phase to a class of intriguing cerium compounds whose characteristics are determined by strong electronic correlations.

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