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Some physical properties of the perovskite-like phases $AlSr_2LnCu_2O_x$

E.P. Khlybov [a,b], G.M. Kuz'micheva [c], T. Palewski [b], P.W. Klamut [d], J. Warchulska [b], T. Mydlarz [b], I.N. Afanas'ieva [c]

[a] *Institute for High Pressure Physics, Russian Academy of Sciences, 142-092 Troitsk, Moscow Reg., Russia*
[b] *International Laboratory of High Magnetic Fields and Low Temperatures, 95 Gàjowicka Str., 53-529 Wroclaw, Poland*
[c] *Moscow State Academy for Fine Chemical Technology, Vernadski Prospect 86, 117-571 Moscow, Russia*
[d] *Institute of Low Temperatures and Structural Research, Polish Academy of Sciences, 2 Okolna Str., 50-950 Wroclaw, Poland*

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Abstract

Polycrystalline samples of the $AlSr_2LnCu_2O_x$ compounds with perovskite-like crystal structure were synthesized. The type of the crystal structure and the lattice parameters of the main phase were determined. None of the phases reveals superconducting properties. The studies of the magnetic properties of the cuprates mentioned above suggest the presence of magnetic ordering in some of these compounds.

Keywords: Cuprates; Crystal structure; Magnetism; Electric properties

1. Introduction

At the present time in many laboratories there is a great deal of effort going into the search for new high temperature superconductors (HTSC) with perovskite-like structure. In searching for new HTSC we have investigated a number of phases with perovskite-like structures. Among them there were cuprates with general formulae M–Sr–Ln–Cu–O where M = Al or Ga and Ln = rare earth element. If the composition of such ceramics can be represented by the formula $AlSr_2LnCu_2O_x$ with value of x between 6 and 7, these phases can crystallize into two similar structures depending on the type of the Ln cation and the synthesis conditions: the so called 1212 type, where the Al cations are placed in a tetragonal arrangement and the 1212* type, where the Al cations are placed in a distorted octahedron [1]. It seemed interesting to study their structural, magnetic and electric properties.

2. Experimental

The samples were obtained by annealing well homogenized mixtures of the appropriate oxides (Ln_2O_3, Al_2O_3, SrO and CuO) during 4–20 h at temperature 940–1080 °C. Some of the samples were additionally annealed several times to achieve a single-phase composition. The diffraction analyses (qualitative and quantitative ones) were performed with a "Geigerflex" diffractometer with $Cu_{K\alpha}$ radiation using a curved graphite monochromator. The lattice parameters of the samples were calculated by a standard method of high precision for angles (2θ) between 20° and 140°. The d.c. magnetic susceptibility and isothermal magnetization measurements were carried out using a balance magnetometer (magnetic fields up to 0.428 T) and a spring magnetometer (magnetic fields up to 10 T). The a.c. magnetic susceptibility was measured with a Lake Shore a.c. susceptometer (magnetic field to 1 T) between 4.5 K and room temperature.

3. Results and discussion

We prepared the series of perovskite-like compounds $AlSr_2LnCu_2O_x$ where Ln represents Y or one of the rare-earth elements (except Pm). The X-ray study of these ceramics revealed that the phases $AlSr_2LnCu_2O_x$ form a morphotropic series. For Ln = La–Tb(Y) the phases have the crystal structure of the 1212* type and for Ln = Dy(Y)–Er they have the crystal structure of

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the 1212 type [1]. In the case of Ln = Tm–Lu only (Al,Cu)$Sr_2LnCu_2O_x$ phases were obtained with a statistical distribution of Al^{3+} and Cu^{2+} in the octahedral positions of the 1212 type or in the tetrahedral position of the 1212* type. The occupation of the octahedral and tetrahedral positions by the Al^{3+} cation may be estimated according to formulae presented in Refs. [1–3]. It is seen from Fig. 1 that the lattice parameters for the various series are somewhat different.

It was found that in the intermediate case of $AlSr_2YCu_2O_x$ phase, the 1212* type is formed after fast cooling of the sample whereas the 1212 type crystal structure is formed during slow cooling. A prolonged annealing of $AlSr_2YCu_2O_x$ samples with the 1212* type crystal structure at temperature $T > 1100$ °C leads to the formation of the $AlSrYCuO_5$ phase where the Al cations regularly occupy tetrahedral and octahedral positions with a crystal structure slightly different from the one mentioned above. It is interesting to note that samples with this structure do not reveal magnetic ordering between 4.2 and 300 K. A prolonged annealing of $AlSr_2YCu_2O_x$ with Al^{3+} in the octahedral position of the 1212 crystal structure results in the formation of the (Al,Cu)$Sr_2Cu_2O_x$ phase with Al^{3+} and Cu^{3+} statistically occupying in octahedral positions. These transitions confirm the fact that the $AlSr_2YCu_2O_x$ phase with 1212* or 1212 crystal structure is at the limit of stability in such a type of crystal structure [1].

The temperature dependence of the d.c. susceptibility for all $AlSr_2LnCu_2O_x$ samples in which the Ln component is magnetic showed only paramagnetic behaviour. This may be attributed to the presence of rare-earth cation in them. However, detailed investigations (also measurements of the a.c. susceptibility) of $AlSr_2YCu_2O_x$ and $AlSr_2LuCu_2O_x$ in which the Ln component does not carry a magnetic moment showed the presence of magnetic ordering (see Fig. 2). In the case of magnetic Ln cations such as Gd, Tb or Yb possible maxima in the thermomagnetic curves are probably obscured by the strong paramagnetic contribution of the rare-earth cations (see Fig. 3). The temperatures of the maxima in the thermomagnetic curves found directly (for Ln = Y or Lu) or after the differentiation of such curves (for Ln = Tm and Yb) occur between 12 K and 22 K. It is very probably that magnetic ordering may be attributed to magnetic interactions between the cuprum ions. Similar interactions between cuprum ions have been found, for example, in $Y_2Cu_2O_5$ [5].

The d.c. susceptibility measurements of a $AlSr_2LuCu_2O_x$ sample at high magnetic fields (up to 7

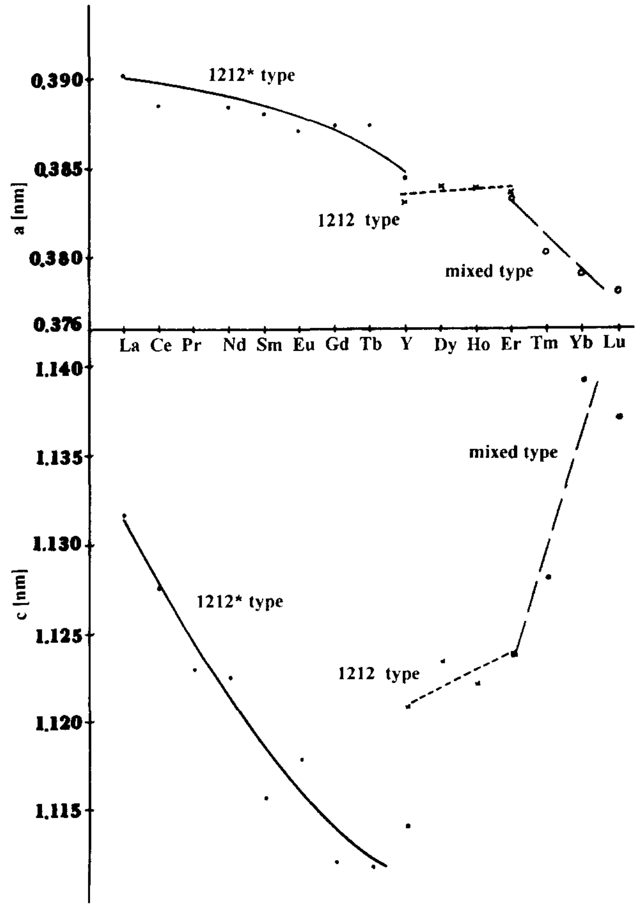

Fig. 1. The lattice constants of the compounds with the 1212 and 1212* type crystal structure.

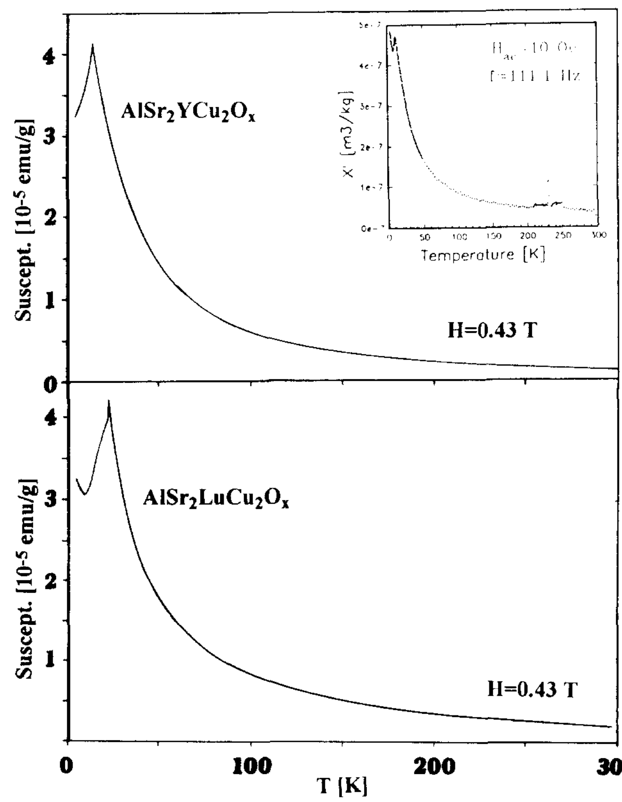

Fig. 2. The temperature dependence of the d.c. and a.c. (see insert) susceptibility for $AlSr_2YCu_2O_x$ sample, and the temperature dependence of the d.c. susceptibility for the $AlSr_2LuCu_2O_x$ sample.

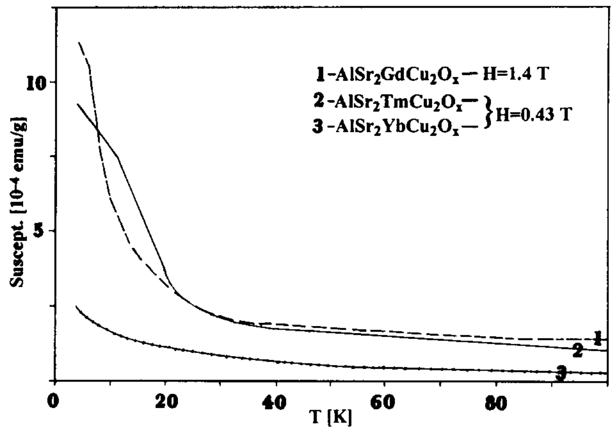

Fig. 3. The temperature dependencies of the d.c. susceptibility for some $AlSr_2LnCu_2O_x$ samples.

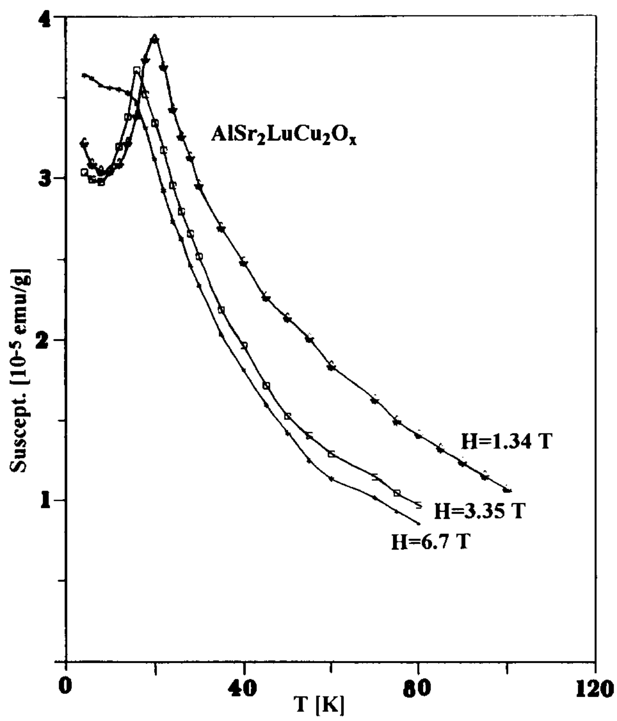

Fig. 4. The temperature dependencies of the d.c. susceptibility for the $AlSr_2LuCu_2O_x$ sample at different magnetic fields.

T) indicate that the magnetic transition is displaced towards lower temperatures (see Fig. 4). Moreover, the temperature dependencies of the susceptibility (see Fig. 4) suggest the existence of a metamagnetic transition at magnetic fields about 6–7 T. Similar metamagnetic transition were found in $Y_2Cu_2O_5$ cuprate [6].

Electrical resistivities of the samples were measured by a d.c. four-probe method. The d.c. current density, applied to the sample, never exceeded 10 A cm^{-2}. Values of R were found to extend over more than 7 orders of magnitude. Unfortunately, the phases under study do not reveal any superconducting properties. The temperature dependence of their resistances can be described by the equation: $R(T)=R_0 \exp(T_0/T)^{\alpha}$.

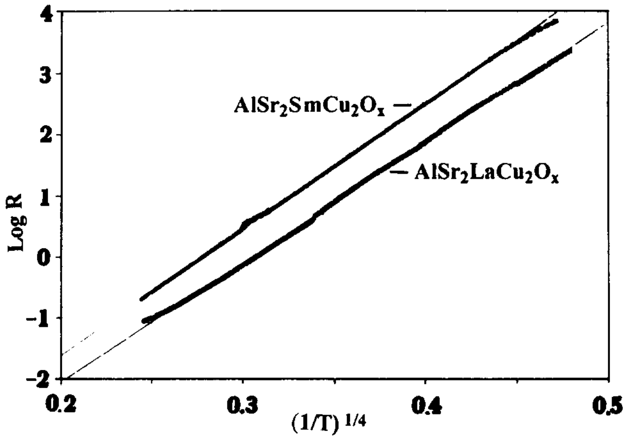

Fig. 5. The electrical resistivity (log$R$) for $AlSr_2SmCu_2O_x$ and $AlSr_2LaCu_2O_x$ samples as a function of $T-1/4$.

In the case of variable range hopping (VRH) the value of α depends on both the dimensionality and the density of states at the Fermi level. The VRH model predicts the value $\alpha=1/4$ for an electron gas in 3-dimensional (3D) systems and $\alpha=1/3$ in 2-dimensional (2D) systems. Other values of α concern the effect of correlation between electrons. In Fig. 5, we have plotted $\log R$ vs. $T-1/4$ for some samples belonging to the series $AlSr_2LnCu_2O_x$.

The results presented above show that the magnetic properties of the $AlSr_2LnCu_2O_x$ series seem to be very interesting and that more detailed investigation is needed to fully understand the observed phenomena.

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