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Colossal electric conductivity in Ag-defect $Ag_5Pb_2O_6$*

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The Byström–Evers compound $Ag_5Pb_2O_6$ was annealed at 500–540 K under a flow of electric current which results in a textured structure and anisotropic colossal electric conductivity (>10^9 Ω^{-1} cm^{-1}) between 210 and 525 K. The related physical properties are primarily governed by dissociation of Ag from *c*-axis channels and lattice strains, which in turn depend upon electric current.

1 Introduction

In previous papers [1, 2] the Pb–Ag–C–O system has been reported as a possible carrier of superconductivity (SC) which extends up to room temperature (RT). More detailed analysis of data leads to the conclusion that the Byström–Evers (BE) compound $Ag_5Pb_2O_6$ [3] is responsible for the properties reported in [1], as well as for properties appearing in an alternative phase discussed in the present paper.

Originally $Ag_5Pb_2O_6$ was prepared in the trigonal form by hydrothermal synthesis [3], while Jansen and co-workers [4–6] prepared the BE compound from PbO_2 and Ag_2O in a solid-state reaction proposing the hexagonal structure shown in Fig. 1a. $Ag_5Pb_2O_6$ consists of channels stretched along the hexagonal *c*-axis (Fig. 1b) and filled with two Ag(1) atoms per unit formula. In order to differentiate between the two types of Ag cations in the BE compound, a more suitable unit formula, $Ag_2[Ag_3Pb_2O_6]$, may be proposed.

2 Results and discussion

Preparation of the BE phase $Ag_2[Ag_3Pb_2O_6]$ was carried out with PbO_2 and Ag_2O mixed in the atomic proportion Ag/Pb = 5/2 using a magnetic stirrer and benzene. The PbO_2 contained traces of H_2O visible by the infrared (IR) technique but undetectable by conventional thermogravimetric (TG) analysis with sensitivity higher than 0.02 mol%.

The mixed powder was then fused for 100 h at 620 K and a pressure of 200 bar O_2. TG decomposition in air to Pb_3O_4 + Ag at 723 K and subsequent decomposition of Pb_3O_4 to PbO at 793 K (Fig. 2, inset) revealed the unit formula $Ag_2[Ag_3Pb_2O_6]$. X-ray diffraction angles and relative intensities correspond to those cited by Jansen and co-workers.

Heating of the BE phase in air, nitrogen or *in vacuo* results in transformations at 550 and 582 K, as is shown by differential thermal analysis (DTA) (Fig. 2) recorded from a pellet of weakly compacted powder (p ~ 30 bar). An annealing at 523 K in air for 48 h results in a partial release of elementary silver, which is confirmed by X-ray analysis and by visual identification of small silver grains. No traces of

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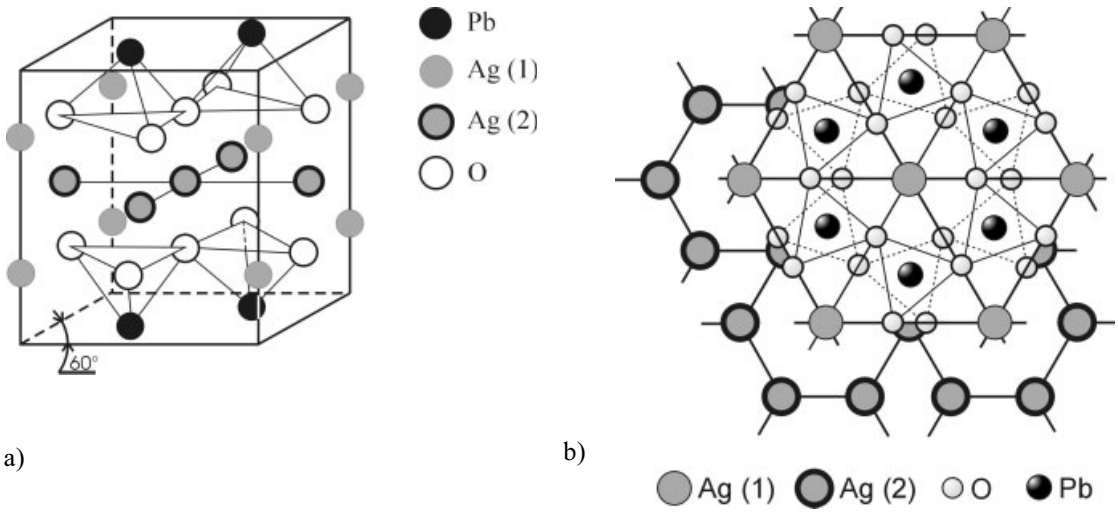

Fig. 1 a) Unit cell of $Ag_2[Ag_3Pb_2O_6]$; b) *c*-axis projection of the unit cell of $Ag_2[Ag_3Pb_2O_6]$.

Pb_3O_4 were recorded which excludes the possibility that silver evolves from the decomposition of the BE compound. When a higher uniaxial stress (about 1500 bar) is applied to the BE powder silver is removed from the compound up to $\beta > 0.30$, with the basic hexagonal structure preserved.

The four-probe electric resistance was measured in a conventional way using 100 μm gold wire and silver paint. The pellet ($5 \times 5 \times 0.4$ mm^3) was prepared by compression ($p \sim 22$ bar) of the BE powder and is shown in the inset of Fig. 3. Heating was performed in air under a dc current of 100 mA with current contacts connected to A–B and voltage contacts to C–D. The pellet was annealed at 523 K for 24 h and subsequently cooled to RT. The reheating is followed by a decrease of electric resistance at $T_D = 345$ K to less than 10^{-7} Ω (Fig. 3), which is the ultimate resolution of our dc resistance measurement. This colossal electric conductivity (CEC) state persists up to 525 K when a partial deterioration appears which manifests as a lower temperature (450 K) of recovery of the CEC state by cooling to RT.

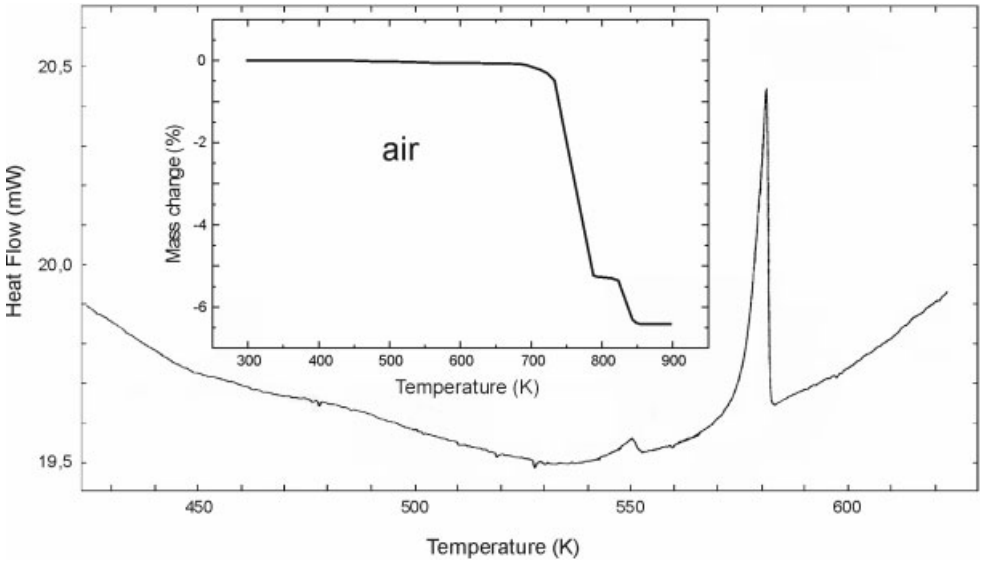

Fig. 2 Differential thermal analysis (DTA) of $Ag_2[Ag_3Pb_2O_6]$ recorded in 1 bar N_2. Inset shows the thermogravimetric decomposition curve of $Ag_2[Ag_3Pb_2O_6]$ recorded in air.

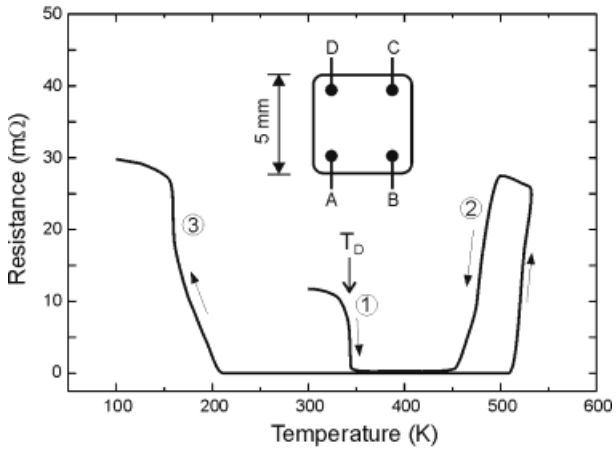

Fig. 3 Temperature dependence of the electric resistance of Ag-defect sample $Ag_{2-\beta}[Ag_3Pb_2O_6]$ heated from RT (1) up to 525 K (2), and then cooled to 100 K (3). Inset shows specimen arrangement with electric contacts glued with silver paint.

Based upon repeated preparations the main characteristic of the CEC state is the downturn temperature T_D which exclusively depends on strains. After cooling to RT and pulling of the holder with sample in free air the CEC state was manifested, under flowing current, over the next three months, independent of the interchange of electric and voltage contacts. In parallel tests an interchange of current contacts to A–D and voltage contacts to B–C revealed normal electric resistance of 0.12 Ω which increased up to 0.55 Ω after 3 months of exposure to air, and the cited anisotropy also appeared after interchange of B–C (current) and A–D (voltage) contacts. It should be borne in mind that deterioration of the CEC state at 525 K has nothing in common with the classic transition from superconducting to normal state but it should be looked upon as a result of the appearance of another high-temperature structural phase. Cooling below RT results in a reversible deterioration of the CEC state near 210 K which is also the lowest T_D recorded by the four-probe resistance measurement. By heating to RT and switching off the current the pellet undergoes, in four days, destruction by self-pulverisation. It should be noted that small Ag grains were visible between the current contacts and this might be included in the scheme of mutual dependence of the CEC state, Ag dissociation and driven electric current strength. It should be pointed out that an anisotropic textured state was also induced by annealing under flowing ac currents (230 cycles per second) supplied from a lock-in amplifier.

Part of the pellet considered in Fig. 3 was mounted in a microwave cavity (9.3 GHz). The temperature dependence of the inverse $2Q$ factor, which scales microwave resistance, is shown in Fig. 4. The sample was first cooled to 90 K and than heated at a rate ~1 K min^{-1}. Decrease of the microwave resistance is clearly visible at T_D = 210 K, and is in fair agreement with our four-probe resistance data, as shown in Fig. 3. By repeated cooling–heating cycles conversions to normal and CEC states took place, as shown in Fig. 4. Application of a magnetic field up to 8 T revealed an absence of field dependence of the microwave resistance in the CEC state.

An investigation of microwave absorption in modulated magnetic field (MAMMA) pointed out an absence of characteristic absorption hysteresis which contradicts the results reported in [2], and calls for attention to be paid to at least two possible modifications of BE samples exhibiting independently classical superconductivity and the CEC state.

Anisotropic electric properties induced by electric currents at elevated temperatures suggested an experimental set-up consisting of a metal tube filled with BE powder. We used a copper tube with outer (OD) and inner diameters (ID) of 4 and 2 mm, respectively. The tube was filled to 18% of theoretical density of the BE phase (8.92 g cm^{-3}) and then extruded to OD = 1.5 mm and ID = 0.62 mm. An empty tube of similar size connected in series with the filled one was used as a reference, and electric contacts were realised by screw-tight fittings. Voltage drops at temperature T of the filled and empty tube are denoted as $V_S(T)$ and $V_R(T)$, respectively, whereas the values at RT are denoted as $V_S(0)$ and $V_R(0)$. A dimensionless coefficient $K = V_S(T)V_R(0)/V_R(T)V_S(0)$ was plotted against temperature as shown in Fig. 5. A decrease of the resistance of the BE-filled tube on heating from RT is evident (Fig. 5, curve a),

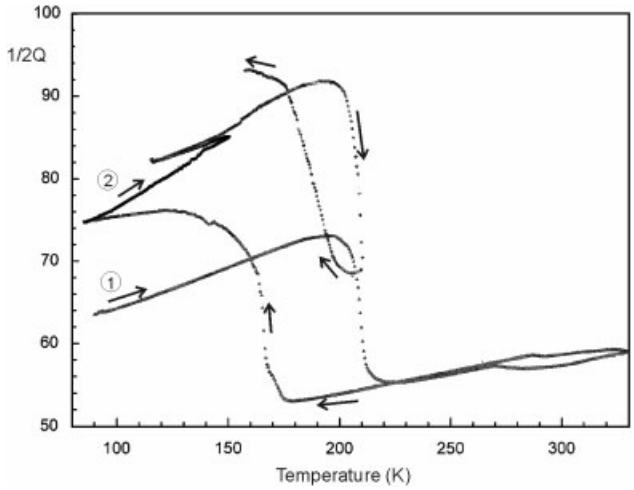

Fig. 4 Temperature dependence of the inverse microwave $2Q$ factor of the sample of Fig. 3 heated from 90 K (1) up to 330 K, then again cooled to 90 K and reheated to 220 K (2).

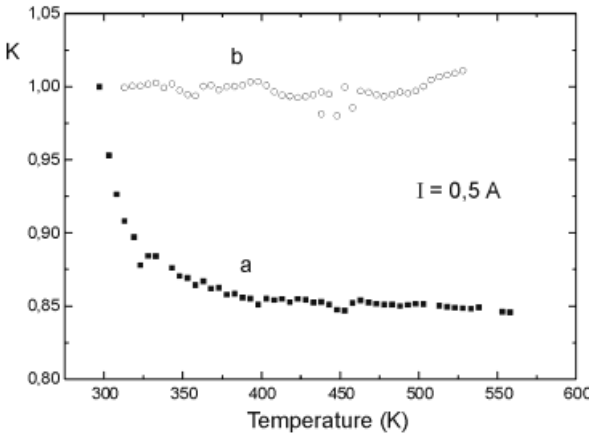

Fig. 5 Temperature dependence of the dimensionless K factor (see text for explanation); (a) copper tube (OD = 1.5 mm, ID = 0.62 mm) filled with the BE powder; (b) empty copper tube of similar size. Resistance measurement current was $I = 0.5$ A.

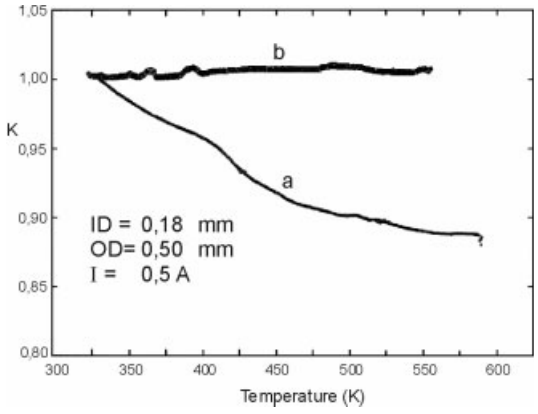

Fig. 6 Temperature dependence of the dimensionless K factor (see text for explanation); (a) copper tube (OD = 0.5 mm, ID = 0.18 mm) filled with the BE powder; (b) full cross-section copper wire of similar size. Voltage contacts were realised with silver paint. Resistance measurement current was $I = 0.5$ A.

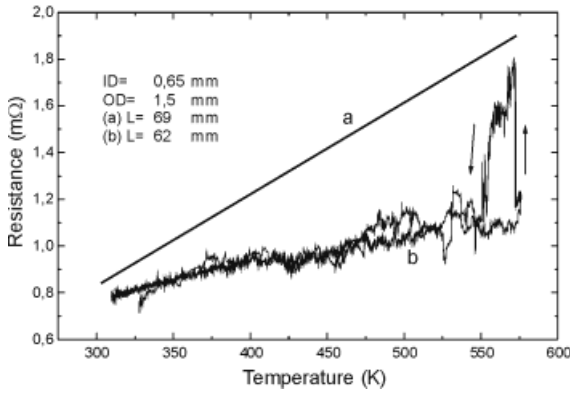

Fig. 7 Temperature dependence of the electric resistance (I = 0.5 A); (a) copper tube (OD = 1.5 mm, ID = 0.62 mm) filled with the insulator Pb_3O_4; (b) tube of similar size (in series with the former) filled with BE powder.

which shows a good correspondence with the decrease of resistance at T_D = 345 K shown in Fig. 3. A net resistance along the wire is a result of interruptions in the powdered core as a result of the low filling factor. The filled tube was then replaced by another empty tube of similar size and the corresponding coefficient K was plotted against T (Fig. 5, curve b).

Figure 6 (curve a) shows the temperature dependence of the dimensionless factor K for the tube filled with BE powder as above, but with OD = 0.5 mm and ID = 0.18 mm, and Fig. 6 (curve b) for the case when the filled tube was replaced by the full cross-section copper wire. Note that voltage contacts were realised using silver paint.

In the next experiment a BE-filled tube was heated under a 0.5 A dc current up to 510 K and then quenched in cold water. Reheating was again performed under 0.5 A and Fig. 7 shows the temperature dependence of the electric resistance of extruded copper tubes: curve a when filled with the insulator Pb_3O_4 and curve b when filled with BE. An increase of the resistance of the BE-filled tube at 568 K to that of the tube filled with Pb_3O_4 is evident. Cooling re-established the CEC state at 548 K. At RT the resistance was nearly 0.6 times that before heating, but was partly recovered over time to the initial value. A rather strong noise visible on the voltage contacts usually precedes a complete loss of the resistance above RT in the copper tube filled with BE powder. The electric resistivity calculated from the cross-section and length of the BE core at 523 K is nearly 3 times smaller than that of silver, although with regard to the low filling factor such a calculation is an overestimate of the resistivity of the BE phase. In addition, tubes equipped with a concentric copper stud 1 mm in diameter and filled with the BE phase in the space between the stud and the inner tube wall show an absence of CEC when the voltage is measured on the stud and current contacts are attached on the outer tube. This means that the CEC is confined to a thin layer of the BE phase on the inner wall, i.e. conductivity is induced by a tangential interaction of the BE phase and electric current flowing in the copper.

3 Conclusions

It may be summarised that: (1) the BE phase undergoes transformations at temperatures of 550 and 582 K, not reported in previous publications; (2) annealing at 523 K results in a partial release of silver from c-axis channels; (3) dissociation at 523 K under flowing current results in a textured structure with high anisotropy of electric resistance; (4) there is a close interdependence of strain, dissociation level of silver and electric current; (5) an absence of magnetic field dependence of microwave resistance data, as well as an absence of MAMMA effect indicate an alternative conclusion to those reported in [2]. Based upon recent experience both effects observed in the BE phase critically depend on strains and related silver defects. To summarise the listed observations, both effects may be recognised, in some instances, as two forms of the same, as yet unknown, phenomenon.

Efficient control of the strain and dissociation is a decisive factor in further research which will shed more light on the physical and chemical properties of the BE compound.

Note added in the proof

The wire sample (OD = 0.5 mm) from Fig. 6a extruded to OD = 0.20 and ID = 0.075 mm exhibits a temperature independent dimensionless factor $K = 0.682 \pm 0.05$ between 77 and 703 K when BE phase decomposes and $K = 1$, that is, the slopes of the temperature dependent resistances of the empty and BE filled tubes are identical, which in turn means that parts of Cu tube are short circuited by BE phase exhibiting CEC between 77 and 703 K.

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