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Thermoelectric properties of Au-based metallic glass at low temperatures

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Thermoelectric properties of $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ glassy alloy have been studied using electrical resistivity, thermal conductivity and Seebeck coefficient measurements over temperature range 2–390 K. At heating, resistivity ρ decreases in a power-law manner from residual value $\rho_0 \sim 150\,\mu\Omega\cdot cm$. The temperature coefficient of resistivity, $\alpha = \rho^{-1}(\partial\rho/\partial T)$, is rather small and varies non-monotonously. Thermal conductivity κ rises linearly at low temperatures; it exhibits a plateau-like feature and sharply increases at elevated temperatures. Seebeck coefficient S increases with temperature and exhibits a characteristic "knee" feature. At elevated temperatures, S increases linearly with temperature but with a different slope. It total, thermoelectric properties of Au-based glassy alloy demonstrate behaviour of a highly disordered system in a most pronounced manner.

Unique physical properties of bulk glassy alloys, i.e. high strength and hardness, large elastic strain limit and corrosion resistance, are quite attractive for a wide range of applications [1]. The first bulk glassy alloy (or metallic glass), namely Au–Si, was produced by rapid solidification of the melt in 1960 [2]. Partial substitution of Si by Ge have led to improved glass-forming ability [3] and later on, other noble metals based metallic glasses were produced [4]. However, all these binary alloys showed a poor glass-forming ability and lacked stability at elevated temperatures. It is recently that a multi-component Au–Cu–Pd–Ag–Si glassy alloy was reported exhibiting excellent glassy properties, low glass forming temperature and good workability [5].

While not directly related to workability, the measurements of thermoelectric properties of bulk glassy alloys provide valuable information on the mechanisms of electrons and ions interactions. Here, we present the measurements of electrical resistivity ρ, thermal conductivity κ, and thermopower S of glassy alloy $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$. Similar to study of Cu-based Cu–Zr–Ti metallic glasses [6] our measurements represent rare case of comprehensive research of transport properties in this class of materials over wide temperature range.

The ingot of a $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ alloy (the composition is given in nominal at. %) was prepared by arc-melting mixtures of high purity elemental metals having more than 99.9 mass. % purity in an argon atmosphere. From this ingot, glassy ribbon samples of about $20\,\mu m$ in thickness and 1 mm in width were prepared by rapid solidification of the melt on a single copper roller at a tangential wheel velocity of 40 m/s. Bulk glassy samples contain a surface layer of crystalline phases [7] and were not used in the present work.

The thermoelectric properties, i.e. electrical resistivity ρ, thermal conductivity κ and Seebeck coefficient (thermopower) S were measured in the temperature range 2–390 K by a four point method using relevant option of "Quantum Design" Physical Properties Measurements System PPMS-9T. The protocol of heat treatment was chosen as follows. Initially, the sample was heated from room temperature to 390 K with the rate 0.5 K/min. It was annealed at 390 K for 2 h. Then the measurements of ρ, κ, and S were carried out at cooling with permanent rate 0.15 K/min. At high temperatures, one point is measured within approximately 23 min. At cooling, this characteristic time decreases progressively. A similar procedure was applied to measure the kinetic properties of $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ alloy during heating. No significant hysteretic phenomena were observed in the series of cooling and heating measure-

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ments, albeit small non-systematic variations in every physical property were detected.

The temperature dependence of resistivity ρ in $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ glassy alloy measured at heating from liquid helium temperature is shown in Fig. 1. The resistivity decreases in a power-law man-

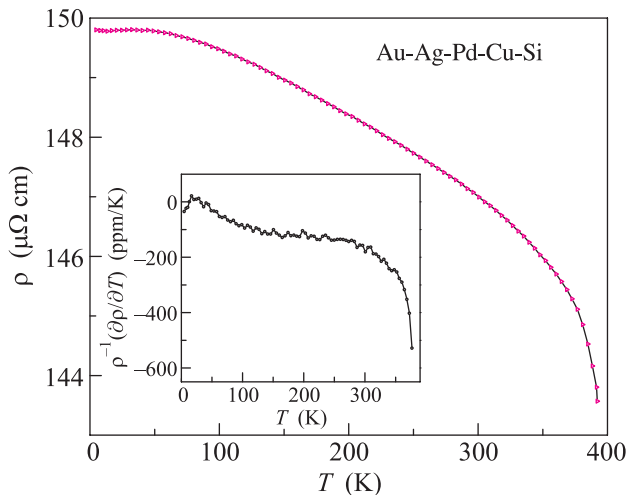Fig. 1. The temperature dependence of resistivity in $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$. The inset – the temperature dependence of the temperature coefficient of resistivity, $\alpha = \rho^{-1}(\partial \rho / \partial T)$

ner from residual value ρ_0 of about $150\,\mu\Omega \cdot cm$ (typical for metallic glassy alloys) at liquid helium temperature. The inset shows the temperature dependence of the temperature coefficient of resistivity, $\alpha = \rho^{-1}(\partial \rho / \partial T)$. At lowest temperatures, the temperature coefficient of resistivity is rather small and varies non-monotonously; it reaches values typical for metallic glassy alloys of about $150\,ppm/K$ and increases rapidly at elevated temperatures. To account for the details of the temperature dependence of resistivity in the intermetallic amorphous alloy, $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$, we follow the general analysis of Cywinsky and Kilcoyne [8].

According to a simple classification scheme of conducting materials, the temperature dependences of resistivity may exhibit different trends. With lowering temperature, the resistivity decreases in metals and exponentially increases in semiconductors. None of these trends is seen in the sample of $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$. It is well known that in a perfect crystal an electron experiences no scattering. The defects of crystal lattice, i.e. impurities, interstitials, vacancies, etc., are the source of scattering leading to the temperature-independent resistivity ρ_0. The temperature-dependent resistivity $\rho_L(T)$ stems from thermal vibrations. Within the Bloch–Grüneisen

formalism, it could be described by a power-low dependence, $\rho_L \sim T^5$, at low temperatures. In the first approximation, ρ_0 and $\rho_L(T)$ are independent from each other and the total resistivity can be written as $\rho(T) = \rho_0 + \rho_L(T)$. This relation known as the Matthiessen's rule is rather well satisfied in numerous polycrystalline alloys. The rapidly quenched amorphous intermetallic alloys, however, are quite far from the ideal crystals. The main difference with the crystals is that the amorphous alloys lack the translational symmetry [9].

As a result, the pronounced crystal disorder leads to significantly enhanced residual resistivity. Indeed, the measured resistivity of $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ is close to that expected when mean free path of the conduction electrons approaches a length scale comparable to the mean interatomic near neighbour distance of about 0.2–$0.35\,nm$ [10, 11]. The deviations from the Matthiessen's rule in $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ are seen in whole temperature range studied. The temperature coefficient of resistivity, $\alpha = \rho^{-1}(\partial \rho / \rho T)$, is rather small $(\sim 10^{-4}\,K^{-1})$ and negative. The $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ glassy alloy, as any other extremely disordered system, exhibits this peculiar and highly unusual behaviour due to the complex interplay of structural scattering processes and quantum corrections arising mainly from weak localization and electron-electron interactions.

The absence of translational symmetry in amorphous alloys necessitates a probabilistic description of the atomic positions in terms of a radial distribution function dominated by short-range atomic correlations. These radial distributions are very similar to those used to describe the structure of liquids. Therefore, to describe the temperature dependence of resistivity in $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ one can use the Faber–Ziman model based on the Ziman theory of conductivity in liquid metals and alloys [12]. The Faber–Ziman theory treats the conduction electrons as plane waves with a wavevector k_F, corresponding to the Fermi momentum, which are coherently diffracted by the amorphous structure. Within this formalism the resistivity ρ is defined by scattering matrix element and the resistivity static structure factor $S^\rho(k)$. The latter is approximately related to the equilibrium structure factor $S(k)$, as measured in conventional x-ray structural studies, through $S^\rho(k) \approx 1 + [S(k) - 1]e^{-2W(k,T)}$. The Debye–Waller factor, $e^{-2W(k,T)}$, introduces the effects of thermal vibrations.

An important feature of the structure factor, $S(k)$, is the large peak at $k = k_p$. For most amorphous alloys $2k_F$ lies close to k_p. In this case, the backscatter-

ing of conduction electrons leads to the characteristic high resistivity. Within the Faber–Ziman approach the negative temperature coefficient of resistivity α is associated with the backscattering condition $2k_{\rm F} \approx k_p$, and reflects the reduction in scattering due to the temperature dependence of the Debye–Waller factor in cases when $S(k = 2k_{\rm F}) > 1$. Basically, these simple qualitative arguments catch main features of the temperature dependence of resistivity in $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$. For $\rho_0 \gg \rho_L(T)$, negative sign of α can be obtained if to introduce multiplicatively the temperature-dependent Debye–Waller factor in Mattheissen's rule, i.e. $\rho(T) = [\rho_0 + \rho_L(T)]e^{-2W(k,T)}$ to account for higher order phonon processes [13].

The temperature dependence of the thermal conductivity κ in $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ glassy alloy is shown in Fig. 2. At lowest temperatures, the ther-
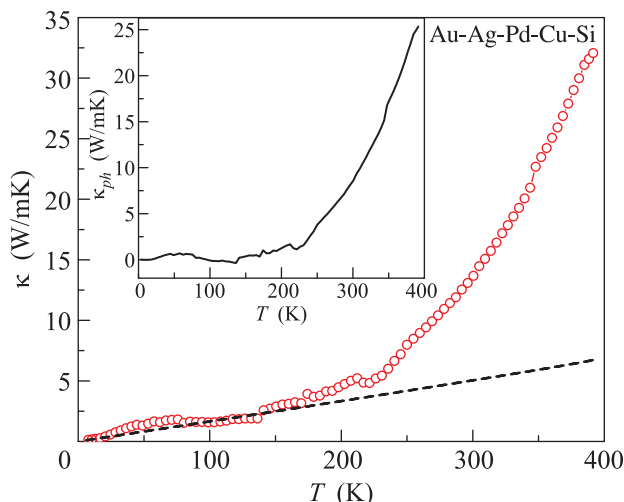

Fig. 2. The temperature dependence of the thermal conductivity in $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ glassy alloy taken at heating. The dashed line represents the electron contribution to overall thermal conductivity. The inset – the temperature dependence of the phonon contribution to overall thermal conductivity

mal conductivity rises almost linearly, it exhibits a plateau-like feature and sharply increases at elevated temperatures. These features are reminiscent of those seen in amorphous insulators where the thermal conductivity is due to phonon heat transfer only [14, 15]. In glassy metals the heat transfer is provided additionally by the conduction electrons. The estimation of electrons thermal conductivity is straightforward using the Wiedemann–Franz law $\kappa_e \rho / T = L$ where the Lorenz number $L = 2.45 \cdot 10^{-8}\,{\rm W \cdot Ohm/K^2}$. Therefore, the electrons thermal conductivity $\kappa_e = LT/\rho(T)$. This quantity is shown by the dashed line in Fig. 2. In

essence, κ_e changes linearly with temperature since the temperature variation of $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ is rather modest. Evidently, up to $T^* \sim 200\,{\rm K}$ the electrons thermal conductivity κ_e constitutes the main part of the overall thermal conductivity. At further increase of temperature, the phonon contribution, κ_{ph}, starts to prevail, as shown in the inset to Fig. 2. The mean free path of the phonons can be estimated with the help of formula $\kappa_{ph} = l_{ph}\nu C/3$, where l_{ph} is the mean free path of phonons, ν is the sound velocity, and C is the specific heat. At critical temperature, T^*, this value is comparable to the mean interatomic near neighbour distance of about $2-3.5\,{\rm \AA}$. Taking into account that the mean free path of phonons reached its natural limit and assuming that the velocity of sound, $ca.\ 3 \cdot 10^3\,{\rm m/s}$, is a gently sloping function of temperature, one can state that the increase of thermal conductivity above T^* is due to the rise of specific heat only.

The temperature dependence of the Seebeck coefficient (thermopower) S in the $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ glassy alloy taken at both heating and cooling processes are shown in Fig. 3. At lowest temperature, the thermopower increases

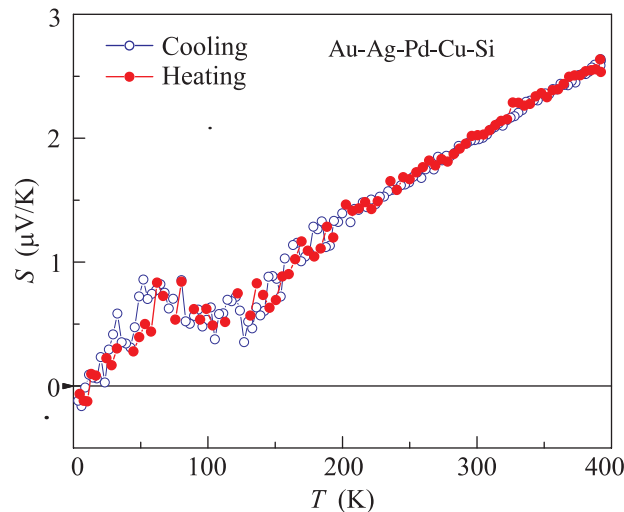Fig. 3. The temperature dependence of the Seebeck coefficient in $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ glassy alloy taken at both cooling and heating

linearly with temperature and exhibits a characteristic for disordered systems "knee" feature. At elevated temperatures, i.e. above $T^* \sim 200\,{\rm K}$, the thermopower increases again but with a different slope.

In $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ the phonon drag contribution to the thermopower S should be negligible owing to the strong phonon scattering in the disordered structure [16]. As in any other non-magnetic metallic

glass, the behaviour of S is almost linear with temperature T over a wide temperature range. The origin of the characteristic "knee" in the $S(T)$ curve at low temperatures is a topic of discussions. The widely accepted concept is that this feature results from the effect of electron-phonon interaction, which renormalizes the electron energy and relaxation time [17]. Moreover, it was shown [18] that the observed temperature dependence of S in a series of amorphous transition metal alloys can be understood as arising from electron-phonon enhancement effects. The enhancement and its temperature dependence were calculated using different models for the interaction of electrons with lattice vibrations and good agreement with the data for several amorphous transition metal alloys was found [19, 20]. The nonlinear thermopower behaviour has also been discussed on the basis of the temperature dependence of the structure factor [21, 22], and of the inelastic electron-electron interaction [23].

Concluding, thermoelectric properties of $Au_{49}Cu_{26.9}Ag_{5.5}Pd_{2.3}Si_{16.3}$ metallic glass have been studied using electrical resistivity ρ, thermal conductivity κ and Seebeck coefficient S measurements over wide temperature range. While basically similar to relevant properties of Cu-based Cu–Zr–Ti glassy alloys the Au-based glass exhibit properties of highly disordered system in a most pronounced manner.

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