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ANOMALY IN THE WIEDEMANN-FRANZ LAW CAUSED BY CHARGE CARRIERS ELECTRON-HOLE CONVERSION

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The aim was to determine which of quasiparticles – the electrons (e) or the hols (h) – is more effective in the diffuse thermal conductivity channel of the high-entropy $Al_{0.5}CoCuCrNiFe$ alloy. The analysis was based on the temperature dependences of the absolute thermoelectric power S(T), electrical resistance R(T), and the scaled thermal conductivity $\chi^*(T)$, the latter of which reflects qualitatively the temperature behavior of the real thermal conductivity $\chi(T)$. It was found that these dependences exhibit specific features in the range of ~250…140 K, with the resistive anomaly sign being "+" and the thermoelectric and thermophysical anomalies signs being "–". Based on the fact that the $Al_{0.5}CoCuCrNiFe$ is an electron-hole conductor, arguments are presented that the S-anomaly reflects the presence of a crossover of latent hole↔electron conversions, resulting in an increase in the concentration C_h of holes charge carriers. Combined with the sign "–" of the thermophysical anomaly, this answers the question posed: in the diffuse heat transfer channel of the $Al_{0.5}CoCuCrNiFe$, holes are less efficient than electrons. The reason for this is revealed by the sign "+" of the resistive anomaly, indicating the ratio of electron and hole mobilities $u_e>u_h$. The theory also posits that the specific electron component of thermal conductivity is greater than the corresponding holes component.

INTRODUCTION

In metals and alloys, the ratio between the electron, χ_e, and phonon, χ_{ph}, components of thermal conductivity χ depends on purity, perfection, the presence of impurities, defects, etc. For "ideal" simple metals, $\chi_e>>\chi_{ph}$, which implies that almost all thermal conductivity is due to electrons. For them, the Wiedemann-Franz law (WF) [1] holds with good accuracy:

$$\frac{\chi}{\sigma T} = const = L\,, \qquad (1)$$

where σ is the specific electrical conductivity and L is the Lorentz constant. The estimate of the value of L for a degenerate electron gas, $L=\pi^2/3(k_B/e)^2=L_0$ (k_B is the Boltzmann constant and e is the electron charge), agrees reasonably well with the experimental values of $\chi/\sigma T$ for many pure metals, and the so-called "ideal" Lorentz number L_0 does not depend on T (see, for example, [2]). When phonons are taken into account, the ratio $\chi/\sigma T$ becomes a function of T, and we say that there is a deviation from the WF law associated with the lattice component χ_{ph}. The fundamental reason for this is the presence of two competing processes: inelastic scattering of electrons by phonons and elastic scattering of electrons on impurities, which vary differently with T. As a result there are anomalies in the $\chi(T)$ and L(T) dependences. Many experimental and theoretical works are devoted to establishing the physical nature of the latter and their positions on the temperature scale depending on the attendant circumstances.

To our knowledge, there are no studies comparing the efficiency of electrons and holes as heat carriers. Suitable conductors for this would be those with two-component electrical conductivity, in which, as a result of electron-hole conversion (EHC), the parameter $C_e(T)/C_h(T)$ (C_e and C_h are the electron and hole concentrations) changes with T non-monotonically and significantly.

In [3–5] it was shown that the high-entropy alloy (HEA) $Al_{0.5}CoCuCrNiFe$, $((N_e/N_h)>1$, where N_e and N_h are the numbers of corresponding charge carriers per unit volume), with electron-hole electrical conductivity, exhibits conversion transformations of free charge carriers below 300 K, which manifest themselves in the form of temperature anomalies of the absolute thermopower $S=S_e-|S_h|$ and electrical resistance R. In an attempt to fill this "thermophysical gap", a comparison of the efficiencies of quasiparticles of different signs as heat carriers was implemented on this alloy. Measurements were carried out of the S(T) and R(T) dependences, which played the role of indicators of the presence of the EHC, and the temperature dependence of a certain scaled thermal conductivity coefficient χ^* was determined, describing qualitatively the real thermal conductivity χ. The reason for introducing χ^* into consideration is that the parallel ultrasonic studies imposed strict requirements on shape and dimensions of the sample. Satisfying these requirements necessitated a qualitative solution, for which a method for identifying temperature anomalies in the $\chi(T)$ dependence for samples of "non-classical" geometry was used [6].

SPECIMENS

The $Al_{0.5}CoCuCrNiFe$ high-entropy alloy Al(4.46), Co(19.48), Cu(21.01), Cr(17.18), Ni(19.4), Fe(18.46) (wt.%, purity ~ 99.9%) was smelted using a proven technology at the NSC "Kharkiv Institute of Physics and Technology" of the NAS of Ukraine. A parallelepiped-shaped sample 5.7×4×4 mm was cut from the ingot using the electric spark method and then annealed at

T=1248 K for 12 h. Metallography revealed the dendritic microstructure, consisting of dendritic bodies (the main part) and interdendritic spaces [7]. According to X-ray diffraction data [7], the cast alloy had a typical two-phase microstructure with a non-uniform distribution of elements. As a result of annealing, the volume of dendrites increased, while the length of the boundaries and the volume of interdendritic spaces decreased. The density of the alloy is 7.979 g/cm^3, the specific electrical resistance is $\rho_{300\ K}$~80 μΩ·cm, $S_{300\ K}$≈+5 μV/K. The sign of S was established by comparison with the sign of the absolute thermoelectric power of copper, which has electronic electrical conductivity (S>0) [8].

METHODS OF THE MEASUREMENTS

All measurements were performed with a stepwise decrease in the distance between the sample, which was in the gas phase of the Dewar with liquid N_2, and the level of the latest. The measurement accuracies of T, R, and U was ≈1 K, ~1% and 10^{-7} V, respectively. The temperature difference ΔT_i between adjacent steady states was measured with a sensitivity of ~10^{-3} K.

R(T) dependence was measured using the two-point scheme at a current of ~1 mA; the potential and current communications were soldered by In in pairs to 4×4 mm faces. Current I flowed along the dendrite axes. The contacting resistances of "In-$Al_{0.5}$CoCuCrNiFe" were not taken into account due to the *s*everal-order-of-magnitude difference in the resistivity of In and $Al_{0.5}$CoCuCrNiFe.

S(T) dependence. Since the proven method for measuring the absolute thermopower S consists of measuring the potential difference ΔU and temperature difference ΔT between the ends of a rod (*l*>>*d*), while the sample under study can be approximated more accurately by a cube, we used an idea, the essence of which is explained in Fig. 1.

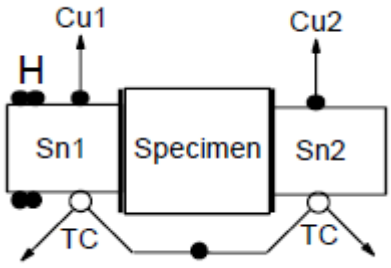

Fig. 1. Schematic diagram for measuring absolute thermoelectric power S (symbols explanations are in the text)

The ends of tin cylinders Sn1 and Sn2 (*d*≈3 mm, *l*≈40 mm) were soldered with In to the 4×4 mm faces of the specimen under study. An electric heater H located at the end of one could generate a heat flux Q along the sequence Sn1→Specimen→Sn2, in the presence of which a temperature difference $\Delta T_{Specimen}$ occurred between the 4×4 mm faces. An insulated Cu-Const thermocouples (TC) junctions were attached to each of the cylinders. There constantan branches were connected, while the copper ones were fed to a circuit of measuring the difference $\Delta(U_{Sn1}\text{-}U_{Sn2})$ which is proportional to $\Delta T_{Specimen}$. To measure $\Delta U_{Specimen}$, copper leads Cu1 and Cu2 leading to the $\Delta(U_{Cu1}\text{-}U_{Cu2})$ measurement circuit. The value of S was calculated using the formula $S=\Delta U_{Specimen}/\Delta T_{Specimen}$. As can be seen, the essence of the modification consists of extending the measuring base with tin elements, which introduce virtually no error in $\Delta U_{Specimen}/\Delta T_{Specimen}$, since the thermal resistances of Sn and the $Al_{0.5}$CoCuCrNiFe alloy differ by several orders of magnitude.

Registration of temperature anomalies χ(T). Due to the impossibility of measuring the classically defined χ, a simplified version of the uniaxial steady-state flow (USF) method [9] was used, which makes it possible to identify temperature anomalies of the χ(T) dependence, leaving the question of quantities out of the equation. The only condition for the correctness of its application is that heat losses in all thermal conductivity channels should change monotonically with a monotonic change in T. This requirement is satisfied, as shown in [6], by the regime of monotonic decrease in the temperature of a sample being in the gas phase of N_2, with strict constancy of the heat flux Q generated by the heater H, Fig. 1. In this case, the scaled thermal conductivity coefficient χ* is determined, which is inversely proportional to the temperature difference $\Delta T=T_1-T_2$ between the ends of the sample: $\chi^*\propto(Q/\Psi)/\Delta T$, where Ψ(T) is the scale factor. In fact, the temperature dependence of the temperature difference $\Delta T_i=T_1(T_i) - T_2(T_i)$ between the ends of the sample must be determined as T decreases from the initial T_0 to the final T_{fin}. In this case, the ratio $\Delta T_0/\Delta T_i=\chi_i^*$ is proportional to the sum of the charge (q) and phonon (ph) components of thermal conductivity: $\chi^* \propto \chi_q(T_i) + \chi_{ph}(T_i)$.

In this study, the coefficient χ* was determined for the case of Q propagation between 4×4 mm faces. The temperature difference $\Delta T_i = T_1(T_i) - T_2(T_i)$ was taken to be $\Delta T_{Specimen}$, calculated from the values $\Delta(U_{Sn1}-U_{Sn2})$, as described in the previous section.

RESULTS

S(T) dependence. Fig. 2 shows a graph of the normalized dependence $S^n(T)\equiv S(T)/S(T_0)$, T_0=300 K, demonstrating the presence of an extended anomaly in the range of ~250…140 K.

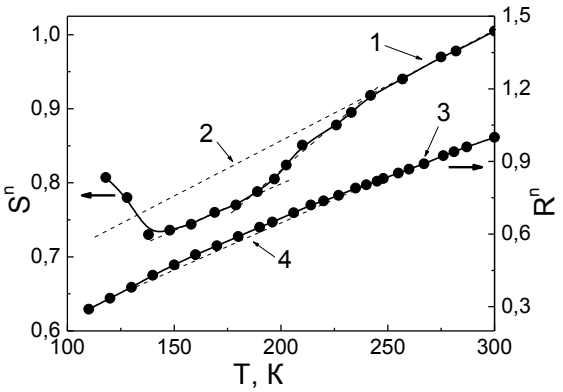

Fig. 2. Solid curves 1, 3 – graphs of the $S^n(T)$ and $R^n(T)$ dependencies; dashed lines 2, 4 – graphs of the $S^n_{BG}(T)$ and $R^n_{BG}(T)$ dependencies

We will determine its nature based on the fact established in [7], according to which the alloy under study does not undergo a structural-phase transformations (SPT) in the range from ~300 to ~100 K. In this case, the alloy should have almost linear dependences R(T) and S(T) [8], which implies an approximate linearity of the change in the carrier scattering cross section with T and a constancy of the numbers of carriers of different signs, $N_e + N_h$ = const. As for the reactions to conversion transformations, in the zero approximation (i.e., without taking into account the change in the effective mass), R is insensitive to them. At the same time, the main indicator of conversion, which is S, can also sense the presence of a "phonon wind" from the warm end to the cold one – the so-called effect of electron drag by phonons [8]. Otherwise, S can have both diffusion (d) and lattice (g) components [8], and of the same sign:

$$S = S_d + S_q . \qquad (2)$$

The sign of the detected S-anomaly – "minus" – is opposite to the sign of S itself ("plus") throughout almost the entire anomalous interval, which excludes Sq. Considering that $S_e(T) > |S_h(T)|$ for all T, it becomes obvious that the S-anomaly is a crossover of latent EHD conversions (since the sign of S does not change) of the "electron → hole" type.

For analysis, we introduce the thermoelectric conversion coefficient $k_S(T) \equiv S^n(T) - S^n_{BG}(T)$. The value of the term $S^n(T) \equiv S(T)/S(T_0)$ is given by experiment, while $S^n_{BG}(T) \equiv S_{BG}(T)/S_{BG}(T_0)$ is a hypothetical normalized $S^n_{BG}(T)$ under the assumption of the absence of EHCs. (Otherwise, for $N_e(T)/N_h(T) \equiv \omega(T)$=const). Next, we note that the straight-line section of curve 1, Fig. 2, in the range of ~300…250 K, were ω(T)=const, makes it possible to obtain a graph of $S^n_{BG}(T)$ throughout the entire anomaly: To do this, we extrapolate the indicated section to the region of low T – dashed line 2 in Fig. 2. The desired graph of the difference $k_S(T) \equiv S^n(T) - S^n_{BG}(T)$ is shown in Fig. 3, curve 1. We pay attention to the localization of the k_S values in the negative region, which indicates an increased of values of C_h in the range of ~250…140 K.

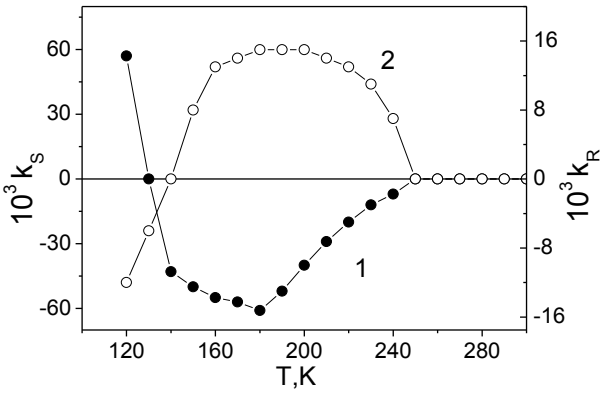

Fig. 3. Temperature dependences of the coefficients of thermoelectric k_S (1) and resistive k_R (2) conversion effects

R(T) dependence. Recall that the nature of the S-anomaly was established based on the absence of SPT in the alloy under investigation. Why is this important? The point is that, in the opposite case, along with the S-anomaly, an in-phase R-anomaly should be present, and then both can be attributed to SPT. To clarify this nuance, the isothermal dependence $R^n(T) \equiv R(T)/R(T_0)$ was measured, T_0 = 300 K (see Fig. 2). In an enlarged scale of the figure, we approximate the hypothetical "conversion-free" dependence $R^n(T)$ with a smooth dashed curve 4 (see Fig. 2), which has the meaning of the $R^n_{BG}(T)$ background. Next, we introduce the coefficient of the resistive conversion effect $k_R(T) \equiv R^n(T) - R^n_{BG}(T)$, the components of which are the values $R^n(T) \equiv R(T)/R(T_0)$ and $R^n_{BG}(T) \equiv R_{BG}(T)/R_{BG}(T_0)$ normalized to 300 K. The graph of the $k_R(T)$ dependence, curve 2, shown in Fig. 3, demonstrates the presence of the same anomalous interval. Two points are important. 1) The values of $k_R(T)$ are positive, the reason for which is undoubtedly the increase in $_{Ch}$. It follows that the holes are scattered by the ionic lattice more strongly than electrons, and the reason for this can only be their larger effective mass than that of an electron. 2) We also note the small magnitude of the resistive effect, which indirectly confirms the invariability of the crystal lattice. As for the reason for the small difference of k_R from zero, it is apparently in the decrease in the average mobility of the entire subsystem of charge carriers due to the electron-hole conversion occurring in its part.

χ*(T) dependence. The graph of the normalized dependence $\chi^*(T) = \Delta T(T_0)/\Delta T(T)$, T_0=300 K, shown in Fig. 4, demonstrates the presence of a negative anomaly in the same range of ~250…140 K, where the S and R anomalies occur.

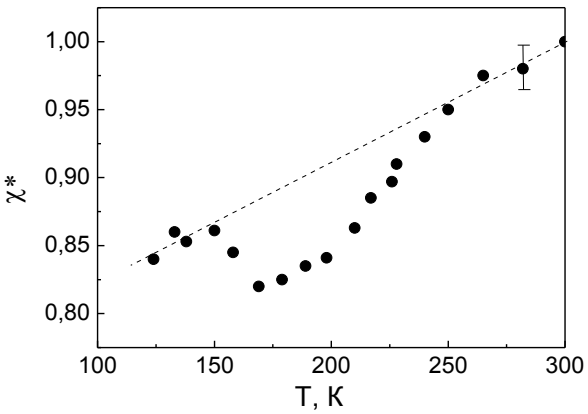

Fig. 4. Temperature dependence of the scaled thermal conductivity coefficient $\chi^* \propto (Q/\Psi)/\Delta T$

Given the smallness of the k_R coefficient, it is appropriate to relate the thermophysical conversion effect to the charge component $\chi_q(T) = \chi_e(T) + \chi_h(T)$. Combined with the increase in C_h, this implies that holes are less effective than electrons in the diffuse thermal conductivity channel.

In conclusion, we present a graph of the temperature dependence of the scaled Lorentz coefficient, L* the expression for which is – by analogy with $L = \chi/\sigma T$ and taking into account the ratio $\sigma = 1/\rho$, as:

$$L^*(T) = \left[\chi^*(T) \cdot R^n(T)\right]/T \ . \qquad (3)$$

The graph of the L*(T) dependence, constructed taking into account the experimental values $\chi^*(T) = \chi(T)/\chi_0$ and $R^n(T) = R(T)/R_0$, is shown in Fig. 5.

We note two points. 1) L*≠const, which confirms the presence of the lattice component χ_{ph}; 2) in the range of ~ 250…140 K, the L*(T) dependence undergoes an anomaly with a minus sign, the reason for which, however, is not as obvious as in the case of the anomaly sign in $\chi^*(T)$, due to the different directions of temperature changes in the factors $\chi^*(T)$ and $R^n(T)$. The issue is resolved by comparing the experimental values of the thermophysical and resistive effects: k_{χ^*max}~(1…2)%, k_{Rmax}~0.2%. From this it is clear that in the presence of both anomalies, the numerator of expression (3) is less than in their absence.

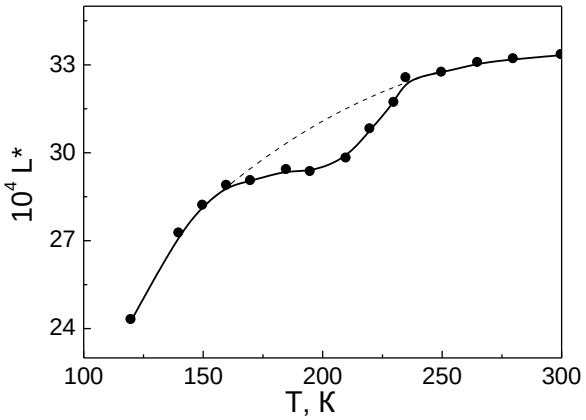

Fig. 5. Temperature dependence of the scaled Lorentz coefficient $L^*(T)=[\chi^*(T)\times R^n(T)]/T$

DISCUSSION

According to theoretical concepts (see [2]), the charge component of thermal conductivity for a simple metal is equal to

$$\chi_q = \left(\pi^2/3\right)\cdot\left(n_q\tau_q/m_q^*\right)\cdot k_B^2\cdot T = A\cdot\left(n_q\tau_q/m_q^*\right), \quad (4)$$

where $A = \pi^2 k_B^2\cdot T/3$; n_q is the density of charge carrier q; $\tau_{qк}$ is the effective scattering time; m* is the effective mass of the q quasiparticle, and k is the Boltzmann constant. For purely electron (q=e) or purely hole (q=h) conductivity, the corresponding χ_q values are: $\chi_e = A_e \times (n_e\tau_e/m_e^*)$ and $\chi_h=A_h \times (n_h\tau_h/m_h^*)$. The ratio of these values for $n_e = n_h$ and $A_e = A_h$ is $\chi_e/\chi_h = (\tau_e/m_e^*)/(\tau_h/m_h^*)$.

Next, we use the experimental fact that the resistive conversion effect is very small, which suggests that $\tau_e \approx \tau_h$. Finally, we obtain $\chi_e/\chi_h \approx m_h^*/m_e^*$. And since $m_h^*>m_e^*$, then $\chi_e>\chi_h$. This is theoretical confirmation of the experimental conclusion that electrons are more efficient than holes in the diffuse heat transfer channel.

CONCLUSIONS

1. The principles of heat and charge transfers in the $Al_{0.5}$CoCuCrNiFe high-energy alloy were studied to establish the comparative effectiveness of electrons and holes as heat carriers. This object was chosen because exhibits electron-hole electrical conductivity, characterized by a change in charge carrier concentration with varying T.

2. It was shown that in the range of ~ 250…140 K, the kinetic coefficients S, R, and χ exhibit anomalies caused by electron-hole carrier conversion, which results in an increase in the hole carrier concentration C_h due to a decrease in C_e. A slight increase in electrical resistance R, which correlates with this, revealed a relationship between the mobilities and effective masses of electrons and holes: $u_e>u_h$ and $m_h^*>m_e^*$, respectively.

3. It is shown that in the range of ~ 100…300 K, the Lorentz coefficient is not constant, indicating that the lattice component of thermal conductivity χ_{ph} is nonzero. At the same time, a slight increase in R due to conversion allows to attribute the thermophysical anomaly entirely to the charge component $\chi_q(T) = \chi_e(T) + \chi_h(T)$.

4. A comparison of the theoretical values of the electron, χ_e, and hole, χ_h, charge components of χ confirms the experimental conclusion: an increase in C_h indeed leads to a decrease in χ due to the larger effective mass of holes. In other words, holes are less effective than electrons in the diffuse thermal conductivity channel of the $Al_{0.5}$CoCuCrNiFe high-energy alloy.

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АНОМАЛІЯ В ЗАКОНІ ВІДЕМАНА-ФРАНЦЯ, СПРИЧИНЕНА ЕЛЕКТРОН-ДІРКОВОЮ КОНВЕРСІЄЮ НОСІЇВ ЗАРЯДУ

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З’ясовувалося, яка з квазічастинок – електрон (e) чи дірка (h) – більш ефективна в каналі дифузної теплопровідності високоентропійного сплаву $Al_{0.5}CoCuCrNiFe$. Основою аналізу були температурні залежності абсолютної термоерс S(T), електроопору R(T) і масштабованої теплопровідності $\chi^*(T)$, остання з яких якісно відображає температурну поведінку реальної теплопровідності $\chi(T)$. Встановлено, що перелічені залежності мають особливості в інтервалі ~250…140 К, при цьому знак резистивної аномалії «+», а знаки термоелектричної і теплофізичної аномалій «−». Спираючись на те, що $Al_{0.5}CoCuCrNiFe$ є електрон-дірковим провідником, приведено аргументи на користь того, що S-аномалія відображає наявність кросовера латентних конверсій виду «електрон↔дірка», в результаті яких збільшується концентрація C_h діркових носії заряду. Разом зі знаком «мінус» теплофізичної аномалії це дає відповідь на поставлене питання: в каналі дифузного переносу тепла сплаву $Al_{0.5}CoCuCrNiFe$ дірки менш ефективні, ніж електрони. Теорія також стверджує, що удільна електронна компонента теплопровідности більша аналогічної діркової величини.