

Low-Temperature Properties of Ordered Cu₃Pd-Based Alloys

N. I. Kourov^a, V. V. Marchenkov^a, V. G. Pushin^a,
A. V. Korolev^a, L. N. Buinova^a, and H. W. Weber^b

^a Institute of Metal Physics, Ural Division, Russian Academy of Sciences,
ul. Sof'i Kovalevskoi 18, Yekaterinburg, 620041 Russia
e-mail: Kourov@imp.uran.ru

^b Atomic Institute of the Austrian Universities, A-1020, Vienna, Austria

Abstract—The effect of atomic disordering and alloying with *d* elements (Fe, Pd, Cu) on the transport and magnetic properties of Cu₃Pd alloys has been investigated at low temperatures ($T < 80$ K) in strong magnetic fields ($H \leq 8$ MA/m). The specific features of the crystal structure and temperature and field dependences of the electrical resistance, magnetoresistance, Hall effect, and magnetic susceptibility of Cu₇₂Pd₂₈, Cu₇₅Pd₂₅, Cu₈₀Pd₂₀ and Cu_{74.5}Pd_{24.5}Fe₁ alloys are discussed.

DOI: 10.3103/S106287380808042X

Wide application of copper–palladium alloys in electronics as electroresistive and electric-contact materials makes topical the problem of determining the role of the mechanisms of charge-carrier scattering and the features of the Fermi surface in the formation of the transport properties of these alloys. Ordered alloys with compositions close to stoichiometric (Cu₃Pd) are of particular interest. Their electronic properties are related to a large extent to the crystallization processes and the presence of antiphase periodic and aperiodic superstructures in them. Investigation of the transport properties at low temperatures ($T < 80$ K) makes it possible to select individual components determining the electroresistive characteristic of the alloys and estimate how they are affected by the degree of atomic order, superstructure imperfection, concentration of the main component, and alloying with *d* elements. In this study, we consider the transport and magnetic properties of the Cu₃Pd alloy with different degrees of atomic order and changes in its properties, depending on the ratio of the main components (alloys with palladium concentrations of 20 and 28 at %) and one-percent alloying with iron.

Electron microscopy and X-ray diffraction analysis show that the Cu₃Pd alloy in the initial, extremely ordered state $L1_2$ has the degree of tetragonality $c/a = 0.986$ and an average grain size of ~ 100 μm [1]. A typical *C*-domain microstructure in the form of packets of parallel, pairwise twinned tetragonal crystals is observed in this alloy. Thermal antiphase domains are also present. The sizes of the tetragonal *C* domains and thermal antiphase domains are varied in a wide range, in particular, their thicknesses range from 50 to 1000 nm and from 20 to 250 nm, respectively. The antiphase boundaries of thermal domains are located mainly over $\{100\}$ cubic planes of the $L1_2$ -lattice. The

splitting of the superstructural reflections along the $\langle 001 \rangle$ direction of the reciprocal lattice corresponds to the layered type of a long-period domain superstructure, fourfold with respect to the corresponding period of the ordered $L1_2$ phase.

The disordered alloy has an fcc structure. It does not contain any thermal superstructural domains and *C* domains; however, superstructural nanoscale $L1_2$ domains with incomplete long-range order are observed in it. No direct proofs of the presence of a periodic antiphase structure were found in the disordered alloy. The specific features of the Cu₃Pd crystal structure and the methods for obtaining extremely ordered and disordered states were described in [1]. The microstructure of the atomically ordered nonstoichiometric Cu₇₂Pd₂₈, Cu₇₅Pd₂₅, and Cu₈₀Pd₂₀ binary alloys and Cu_{74.5}Pd_{24.5}Fe₁ ternary alloy has on the whole the same character. However, the substructure in these alloys is of poorer quality due to the decrease in the size of thermal antiphase and *C* domains, which make an additional contribution to the decrease in the total degree of the alloy long-range order.

The results of the low-temperature resistivity measurements (Fig. 1, table) demonstrate an increase in $\rho(T)$ by a factor of more than 2 in the case of atomic disordering and as a result of alloying of an extremely ordered Cu₃Pd alloy with transition *d* elements (in our case, Pd, Cu, or Fe). This, fairly large increase in $\rho(T)$ is related to the crystal structure transformation and generation of additional local scattering centers (intercrystallite boundaries) for charge carriers. Due to the formation of nanocrystalline states, the density of these centers and the scattering conditions sharply change due to the decrease in the crystallite size. In this case, it is necessary to take into account that a decrease in the crystallite size is accompanied by escape of all defects

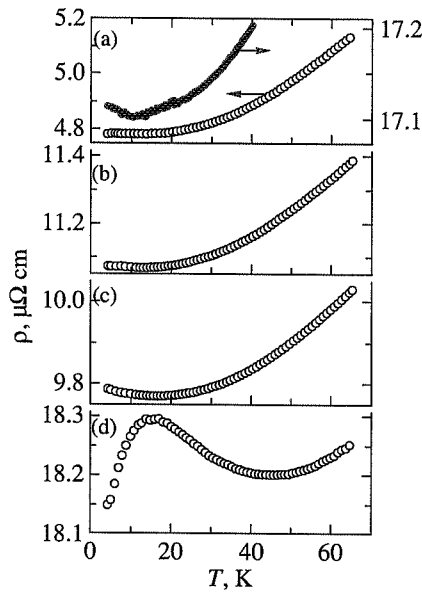


Fig. 1. Temperature dependences of the resistivities of the (a) $\text{Cu}_{75}\text{Pd}_{25}$ (in the \circ) atomically ordered and (\bullet) disordered states), (b) $\text{Cu}_{72}\text{Pd}_{28}$, (c) $\text{Cu}_{80}\text{Pd}_{20}$, and (d) $\text{Cu}_{74.5}\text{Pd}_{24.5}\text{Fe}_1$ alloys. The arrows indicate the coordinate axes.

from the sample bulk to boundaries. The role of the size effect in the significant increase in the resistance of nanocrystalline materials was established by Mayadas and Shatzkes [2].

At the lowest temperatures ($T \leq 30$ K), the ordered Cu_3Pd alloy exhibits a dependence $\rho(T)$ typical of nonmagnetic alloys of transition metals. Along with the temperature-independent component ρ_0 , the resistivity contains the contribution $\rho_{ee} = bT^2$ related to electron-electron scattering, which is enhanced by the charge carrier transfer from the s band to the d band and scattering from spin fluctuations, and the term $\rho_{ph} = cT^5$, which is related to the electron-phonon scattering of carriers at $T < 0.1\theta_D$ ($\theta_D = 323$ K is the Debye temperature [3]). The data in Fig. 1 and the table indicate that the dependence $\rho(T)$ for the Cu_3Pd alloy does not sig-

nificantly change in a longitudinal magnetic field. Only the coefficient b , characterizing the electron-electron scattering, increases. The residual resistance ρ_0 and the electron-phonon component change only slightly.

As a result of atomic disordering and deviation of the alloy composition from stoichiometric (to any side) a shallow minimum arises in the curve $\rho(T)$. For the disordered Cu_3Pd alloy and the alloy with excess palladium, it is retained in the magnetic field $H = 8 \text{ MA m}^{-1}$, whereas excess copper, vice versa, leads to its disappearance. The temperature-dependent part of the resistivity changes most significantly as a result of one-percent alloying of the Cu_3Pd alloy with iron. Figure 1 indicates that, along with the minimum in the dependence $\rho(T)$ at $T \sim 45$ K, a pronounced maximum arises at lower temperatures ($T \sim 15$ K); i.e., the sign of the temperature coefficient of the resistivity changes again. The features of the low-temperature behavior of $\rho(T)$, which were experimentally found in the alloy with % iron, completely disappear even in magnetic fields $H \geq 0.8 \text{ MA m}^{-1}$; in this case, the slope of the $\rho(T)$ curve becomes positive in the entire range of the temperatures studied.

To explain the low-temperature minimum in the dependence $\rho(T)$ for alloys of transition metals, several models are used. In the case under consideration, the most acceptable approaches are the Kondo model [4] and its structural analog [5], which give a negative additive $\rho_K = -a \ln T$. The weak effect of magnetic field on the low-temperature dependence $\rho(T)$ indicates that the structural analog of the Kondo effect is determining for binary alloys [5]. Radically different situation occurs in the $\text{Cu}_{74.5}\text{Pd}_{24.5}\text{Fe}_1$ ternary alloy, which contains, along with nonmagnetic copper and palladium atoms, magnetic iron atoms with a low concentration. In this case, the logarithmic increase in the resistivity is a manifestation of the dynamic nature of the magnetic spin system. The logarithmic increase in $\rho(T)$ with a decrease in the temperature of a ternary alloy disappears not only in a magnetic field but also at a sample transition into a magnetically ordered state near $T \sim 15$ K, where the conditions for spin turnover during electron scattering are absent.

Results of treatment of the temperature dependences of the resistivity using the formulas $\rho(T) = \rho_0 + bT^2 + cT^5$ and $\rho(T) = \rho_0 - a \ln T + bT^2 + cT^5$

Alloy	$H, \text{ MA m}^{-1}$	$\rho_0, \mu\Omega \text{ cm}$	$a, \mu\Omega \text{ cm}$	$b \times 10^5, \mu\Omega \text{ cm K}^{-2}$	$c \times 10^{10}, \mu\Omega \text{ cm K}^{-5}$
$\text{Cu}_{72}\text{Pd}_{28}$	0	11.0947	0.01214	3.957	8.267
	8	11.093	0.01294	4.55	6.256
$\text{Cu}_{75}\text{Pd}_{25}$	0	4.784	0	0.4418	16.52
	8	4.859	0	2.14	14.13
$\text{Cu}_{80}\text{Pd}_{20}$	0	9.815	0.01815	2.685	6.731
	8	9.783	0.003182	1.103	8.027

The magnetic susceptibility data (Fig. 2) indicate the presence of long-range antiferromagnetic ordering in the $\text{Cu}_{74.5}\text{Pd}_{24.5}\text{Fe}_1$ ternary alloy at $T \leq 15$ K. Treatment of these experimental data with the use of the generalized Curie–Weiss law yields the following values: the paramagnetic Curie temperature $\theta_p = -18$ K, the effective magnetic moment $\mu = 1.27 \mu_B$ /formula unit, and the temperature-independent component of the magnetic susceptibility $\chi_0 = -0.88 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$. In the same time, the Cu_3Pd alloy is characterized by the values $\theta_p \sim -1$ K, $\mu \sim 0.2 \mu_B$ /formula unit, and $\chi_0 \sim -1.2 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$, which only slightly vary with the degree of atomic order. The presence of a small effective moment in the nonmagnetic Cu_3Pd compound can be due to the presence of impurity in the sample or polarization of the palladium d band. The large value of the diamagnetic component χ_0 indicates the decisive role of light carriers in the behavior of the electronic properties of the alloys under consideration, which is generally related to anisotropy of the Fermi surface (its fine features). The band calculations [6] indeed show the presence of necks on the Fermi surface of Cu_3Pd in the (110) plane along the Γ – R directions of the first Brillouin zone.

The change in the resistivity in a magnetic field for the alloys under study is shown in Figs. 3 and 4. It can be seen that the longitudinal and transverse magnetoresistances for stoichiometric alloys and those having excess palladium are positive, and the longitudinal $\Delta\rho/\rho$ effect is smaller than the transverse one by only 40–50%. In the extremely ordered Cu_3Pd alloy, the longitudinal and transverse magnetoresistances are proportional to $H^{3/2}$, while in the alloy with 28 at % Pd, with much higher $\rho(T)$, the magnitude of both effects is proportional to H^2 . With a deviation from stoichiometry to the opposite side (in the alloy with 20 at % Pd), the field dependences of the $\Delta\rho/\rho$ effects become more complicated: $\Delta\rho/\rho(H) \sim -aH + bH^{3/2}$. In nonstoichiometric binary alloys, the magnitude of these effects is smaller than in Cu_3Pd . In the iron-containing alloy, the longitudinal and transverse magnetoresistances are negative, have the same magnitude, and linearly depend on field. Figure 4 indicates that, with an increase in temperature of the ordered stoichiometric alloy, both the longitudinal and transverse $\Delta\rho/\rho$ effects decrease. In nonstoichiometric binary alloys, the $\Delta\rho/\rho$ effects have different signs in a wide range of investigated temperatures. With an increase in temperature, the absolute value of $\Delta\rho/\rho$ decreases most rapidly in the $\text{Cu}_{74.5}\text{Pd}_{24.5}\text{Fe}_1$ ternary alloy.

Until now, the transport properties of the alloys under study were considered, in essence, in the single-electron approximation. However, in the alloys with a complex Fermi surface, to which (according to [6]) the objects under study can be assigned, the transport properties can be determined not only by electrons but also holes (positive charge carriers). The nature of charge

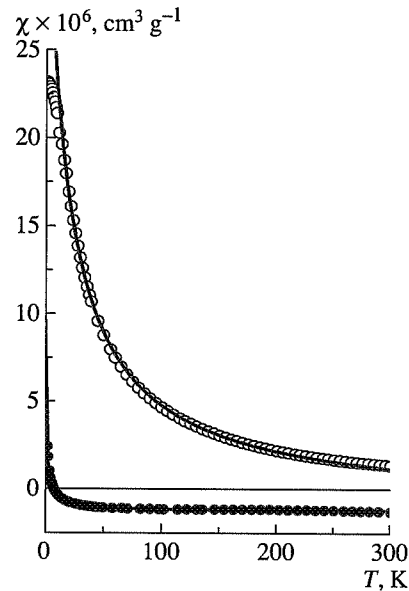


Fig. 2. Magnetic susceptibilities of the atomically ordered (●) $\text{Cu}_{75}\text{Pd}_{25}$ and (○) $\text{Cu}_{74.5}\text{Pd}_{24.5}\text{Fe}_1$ alloys.

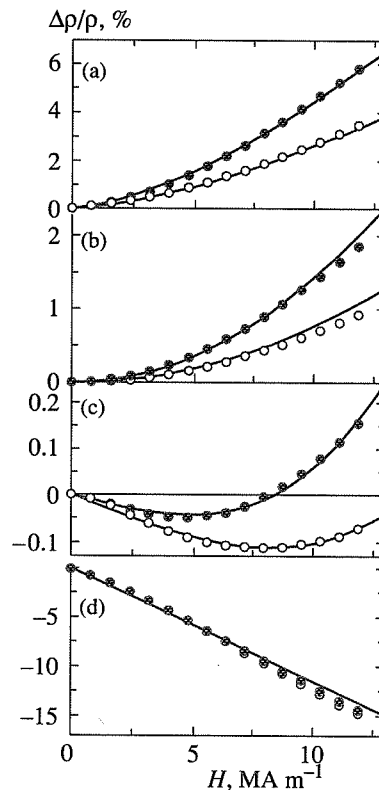


Fig. 3. Field dependences of the (○) longitudinal and (●) transverse magnetoresistances of the alloys studied. The solid lines show the calculated dependences $\Delta\rho/\rho(H)$, which are proportional to (a) $H^{3/2}$ for the $\text{Cu}_{75}\text{Pd}_{25}$ alloy, (b) H^2 for the $\text{Cu}_{72}\text{Pd}_{28}$ alloy and (c) $-aH + bH^{3/2}$ for the $\text{Cu}_{80}\text{Pd}_{20}$ alloy (c) and (d) the linear dependence for the $\text{Cu}_{74.5}\text{Pd}_{24.5}\text{Fe}_1$ ternary alloy.

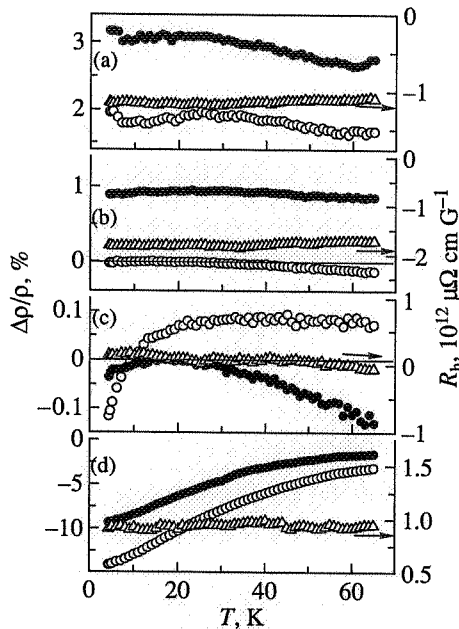


Fig. 4. Temperature dependences of the (Δ) Hall coefficient and (\circ) longitudinal and (\bullet) transverse magnetoresistances for the (a) $\text{Cu}_{75}\text{Pd}_{25}$, (b) $\text{Cu}_{72}\text{Pd}_{28}$, (c) $\text{Cu}_{80}\text{Pd}_{20}$, and (d) $\text{Cu}_{74.5}\text{Pd}_{24.5}\text{Fe}_1$ ordered alloys. The arrows indicate the coordinate axes.

carriers can be found from Hall measurements. In these alloys, at $H \leq 8 \text{ MA m}^{-1}$, the Hall resistivity linearly depends on field; this fact makes it possible to determine with good accuracy the Hall coefficient R_h and its temperature dependence. On the assumption that there are two types of charge carriers, the Hall data (Fig. 4) indicate that, for the Cu_3Pd stoichiometric alloy and the alloy with excess palladium, the main carriers in the entire temperature range studied are electrons, whereas for the ternary alloy with % Fe, such are holes. For the alloy with excess copper, an increase in temperature leads to a change in the sign of R_h , which is most likely to be due to the change in the mobilities of carriers of different type. Apparently, the change in the carrier mobilities leads also to the observed weak temperature dependences of the coefficient R_h for all alloys under consideration.

The investigations performed show that, in the case of atomic disordering of the extremely ordered Cu_3Pd alloy or as a result of its alloying with transition d elements (Pd, Cu, or Fe), a minimum arises at low temper-

atures in the dependence $\rho(T)$, which is related to the Kondo mechanism [4] and its structural analog [5]. This conclusion is confirmed by the presence of a negative logarithmic contribution to $\rho(T)$ and specific features of the behavior of the low-temperature resistivity and magnetic properties in strong magnetic fields.

The fact that the longitudinal and transverse magnetoresistances have comparable magnitudes but different field and temperature dependences (determined by the degree of atomic order and concentration of alloy components) is explained by the existence of two contributions to the $\Delta\rho/\rho$ effects. One of them is due to the rotation of conduction electrons by the Lorentz force under the conditions where the mean free path of conduction electrons is comparable with the Larmor radius or even smaller (see, for example, [7]). The other contribution is caused by the ordering of magnetic scatterers for charge carriers. The Hall data indicate that the presence of two types of carriers with different signs determines the transport properties of the alloys studied. The concentrations and mobilities of these carriers depend on the type of the alloying element and temperature.

ACKNOWLEDGMENTS

This study was carried out according to the plan of the Russian Academy of Sciences (subject nos. g.r. 01.2.006 13392 and g.r. 01.2.006 13395) and supported in part by the Russian Foundation for Basic Research, project no. 06-03-9606, and the Ministry of Education and Science of the Russian Federation (contract nos. 02.51311.3053 and 02.513.11.3197). V.V. Marchenkov acknowledges the support of the Austrian Academy of Sciences.

REFERENCES

1. Kourov, N.I., Pushin, V.G., Korolev, A.V., et al., *Fiz. Met. Metalloved.*, 2007, vol. 103, no. 4, p. 386 [*Phys. Met. Metallogr.* (Engl. Transl.), vol. 103, no. 4, p. 370].
2. Mayadas, A.F. and Shatzkes, M., *Phys. Rev. B: Solid State*, 1970, vol. 1, p. 1382.
3. Sato, Y., Sivertsen, J.M., and Toth, L.E., *Phys. Rev. B: Solid State*, 1970, vol. 1, p. 1402.
4. Kondo, J., *Prog. Theor. Phys.*, 1964, vol. 32, p. 37.
5. Cochrane, R.W., Harris, R., Strom-Olson, J.O., and Zuckerman, M.I., *Phys. Rev. Lett.*, 1975, vol. 35, p. 676.
6. Wilkinson, I., Hughes, R.J., Major, Zs., et al., *Phys. Rev. Lett.*, 2001, vol. 87, 216 401.
7. Volkenshtein, N.V., Startsev, V.E., and Dyakina, V.P., *Phys. Status Solidi B*, 1974, vol. 66, p. K107.