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Electrical Resistivity Studies of Chromium-Rich Chromium-Cobalt Alloys

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The electrical resistivity of chromium-cobalt alloys, containing 0.4, 1.2, 1.7, 2.2, 2.7, 3.5, 4.4, 6.2, and 8.0 at.% cobalt, has been studied as a function of absolute temperature from 4 to 350°K. The Néel point first decreases with increasing cobalt concentration, reaching a minimum at about 1.2 at.% cobalt, then increases to a maximum value at 2.7 at.% cobalt, and then gradually decreases again. At low temperatures the alloys containing more than 2.7 at.% cobalt exhibit a minimum in the resistivity versus temperature plot. This is the first time this phenomenon has been noticed in chromium solid solutions; it appears to have essentially the same origin as in certain other magnetically dilute solid solutions. Electrical magnetoresistivities of the above-mentioned chromium-cobalt alloys have been studied in transverse magnetic fields up to 12 kOe and longitudinal fields up to 60 kOe at 4.2°K. These fields have small influence on the electrical resistivity, which is in sharp contrast with the behavior found in chromium-iron alloys. These results are briefly discussed from the viewpoint of recent theories.

INTRODUCTION

RECENTLY[1–3] it has been found that additions of iron to chromium drastically influence the antiferromagnetic properties of pure chromium. The Néel temperature decreases with iron concentration, and the electrical-resistivity increase just below the Néel point becomes anomalously large when iron enters the chromium lattice. Because of these interesting results, we decided to extend the electrical resistivity studies to other chromium alloys containing ferromagnetic solutes. In this paper we present our results on chromium-cobalt solid solutions. The electric properties of this system, except for the resistivity measurements by de Vries[4] on a sample containing 1 at.% cobalt, have not been determined before.

EXPERIMENTAL CONSIDERATIONS

The chromium-cobalt alloys containing 0.4, 1.2, 1.7, 2.2, 2.7, 3.5, 4.4, 6.2, and 8.0 at.% cobalt used in this study were prepared by arc-melting chromium and cobalt in the same manner as was done with chromium and iron (described elsewhere).[3] Cobalt (J.M. 873), added to chromium (the same stock used before) as a solute, was obtained from Johnson, Matthey, and Company. According to the supplier the following elements (in ppm) were detected by spectrographic techniques: Ni(2), Si(2), Cu(1), Fe(1), Ag(<1), and Mg(<1). The following elements were specifically sought but not detected: Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Cr, Cs, Ga, Ge, Hf, In, Ir, K, Li, Mg, Mn, Mo, Na, Nb, Os, P, Pb, Pd, Pt, Rb, Re, Rh, Rn, Sb, Se, Sn, Sr, Ta, Te, Ti, Tl, V, W, Zn, and Zr. The electrical resistivity ratio $\rho(298°\text{K})/\rho(4.2°\text{K})$ for this cobalt was found to be about 36. After the melting, the ingots were sealed into silica capsules filled with 150 Torr of argon at 298°K, homogenized at 1173°K for 168 h, and then furnace-cooled.

The samples for the electrical resistivity measurements were cut using a wafering machine with a high-speed carborundum disk. The final shape of the samples was obtained by means of a surface-grinding machine. The size of the resistivity samples was about 0.3 cm ×0.3 cm×3 cm.

Electrical resistivity measurements as a function of temperature were made using the apparatus described elsewhere.[5] With this equipment it was also possible to study the influence of transverse magnetic fields up to 12 kOe on the resistivity at different temperatures. In order to learn more about the behavior of the chromium-cobalt alloys, some longitudinal magneto-resistivity studies were performed at 4.2°K in magnetic fields up to 60 kOe. These fields were achieved using a compensated Westinghouse superconducting solenoid with the i.d. of 2 in., o.d. 6 in., and length 16 in. Because of this size bore, four samples mounted in a special sample holder, could be studied at the same time.

EXPERIMENTAL RESULTS

Figure 1 shows the total electrical resistivity, $\rho(T)$, of chromium and chromium-cobalt alloys as a function of the absolute temperature T from liquid-helium temperatures to 350°K. These curves were obtained with increasing temperatures. The plot for pure chromium is that already reported before.[5]

The Néel point (the antiferromagnetic-paramagnetic transition), designated by T_N, in pure chromium shows up as a small minimum in the ρ versus T curve and occurs at 313.0±0.2°K. This minimum, when cobalt is

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added to chromium, first decreases and then again increases with increasing cobalt concentrations. In this respect cobalt is quite different from iron which gradually decrease the Néel temperature of chromium. The resistivity minima, which presumably in chromium-cobalt alloys are also associated with the antiferromagnetic-paramagnetic transitions, are shallow in comparison with those observed in chromium-iron system.[3] The temperatures at which these minima occur for chromium-cobalt alloys are presented in Fig. 2.

Another quite distinct feature observable from Fig. 1 is the formation of a minimum in the $\rho(T)$ versus T curves at low temperatures after a certain concentration of cobalt in chromium is exceeded. The resistivity minimum definitely occurs in 2.7 at.% cobalt alloy at 17.6°K and in all other alloys with higher cobalt content. It is very possible that a minimum also exists at about 13°K in 2.2 at.% cobalt-chromium alloy. However, because of a small irregularity at lower temperatures and the smallness of this minimum, its existence cannot be stated with complete certainty. The development of these low-temperature resistivity minima in the chromium-cobalt solid solutions is more clearly presented in Fig. 3. The percentage intervals are indicated in Fig. 1 to make it easier to judge the relative depth of the minima. Figure 4 gives the concentration dependence of the temperature at which the resistivity minimum occurs ($T_{\min}$).

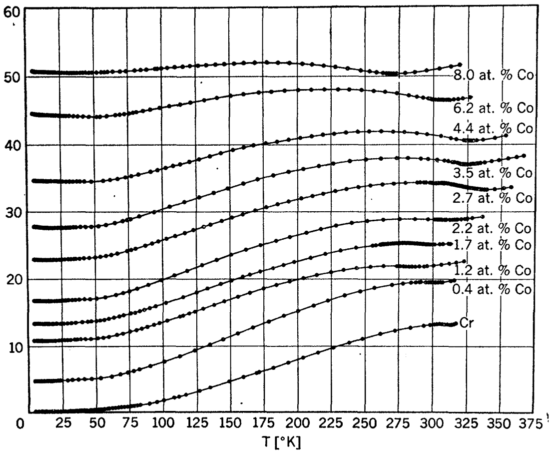

FIG. 1. Total electrical resistivity of chromium-cobalt alloys below 350°K.

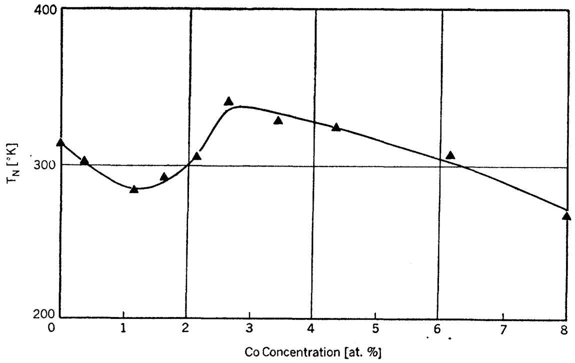

FIG. 2. T_N of chromium-cobalt alloys.

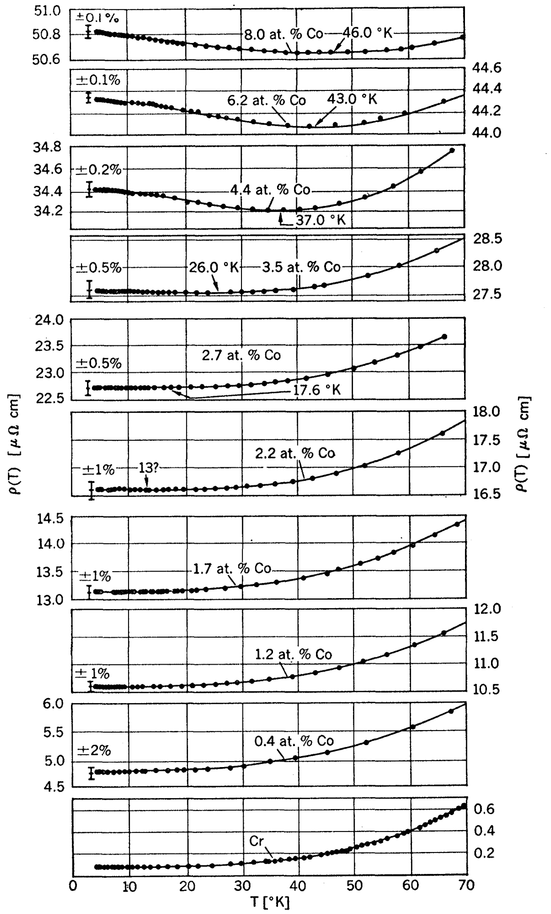

FIG. 3. Total electrical resistivity of chromium-cobalt alloys below 70°K showing the development of the resistivity minimum.

Table I summarizes the quantities T_N, $T_{\min}$, and $\rho(4.2°K)$ for the chromium-cobalt alloys studied in this investigation.

TABLE I. T_N, $T_{\min}$, and $\rho(4.2°K)$ of chromium-cobalt alloys.

Cobalt concentration (at. %)	T_N (°K)	$T_{\min}$ (°K)	$\rho(4.2°K)$ (μΩ cm)
0	313	Absent	0.08
0.4	301	Absent	4.73
1.2	282	Absent	10.60
1.7	291	Absent	13.13
2.2	304	13?	16.61
2.7	339	17.6	22.78
3.5	328	26.0	27.59
4.4	323	37.0	34.39
6.2	306	43.0	44.33
8.0	268	46.0	50.80

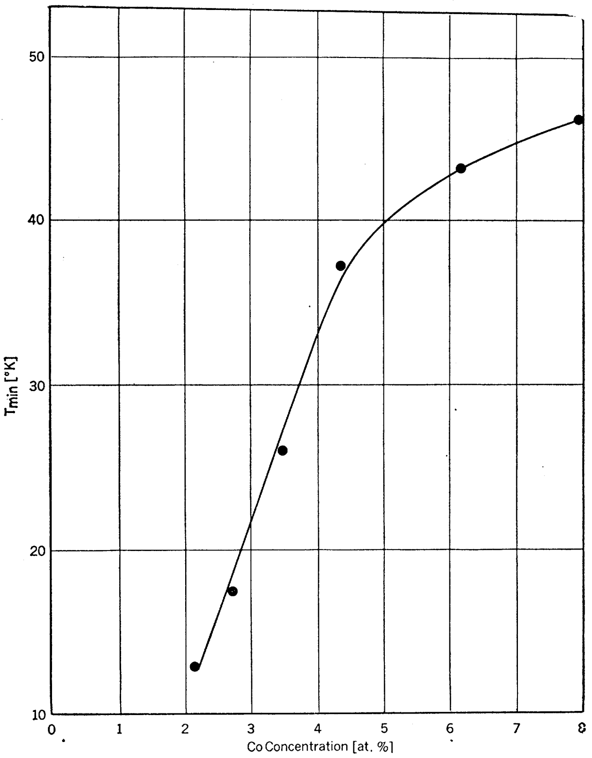

FIG. 4. $T_{\min}$ as a function of cobalt concentration in chromium-cobalt alloys.

The effect of a transverse applied magnetic field $H_\perp=12$ kOe on the total electrical resistivity of the chromium-cobalt alloys at 4.2°K is presented in Fig. 5. The quantity $\Delta\rho_\perp(4.2^\circ\mathrm{K},H)$ represents the difference between the resistivity value at $H_\perp=12$ kOe and $H_\perp=0$ kOe at 4.2°K. Increasing cobalt content rapidly decreases $\Delta\rho_\perp(4.2^\circ\mathrm{K},H)/\rho(4.2^\circ\mathrm{K}, 0\ \mathrm{kOe})$, where $\rho(4.2^\circ\mathrm{K}, 0\ \mathrm{kOe})$ is the zero-field resistivity. Contrary to the observations in the chromium-iron system, this quantity remains positive for all cobalt concentrations studied in this investigation. The influence of longitudinal magnetic fields is essentially similar to those of the transverse fields except for the possibility of very small negative magnetoresistivity in 3.5, 6.2, and 8.0 at.% cobalt alloys at high values of $H_{\parallel}$. Plots of $\Delta\rho^{\parallel}(4.2^\circ\mathrm{K},H)/\rho(4.2^\circ\mathrm{K}, 0\ \mathrm{kOe})$ versus $H_{\parallel}$ for some chromium-cobalt alloys are shown in Fig. 6. The effect of longitudinal magnetic field on pure chromium is presented in Fig. 7.

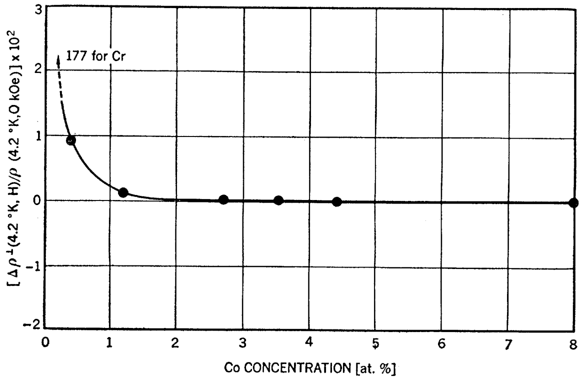

FIG. 5. Transverse relative electrical magnetoresistivity of chromium-cobalt alloys at $T=4.2^\circ$K in $H_\perp=12$ kOe as a function of cobalt concentration.

DISCUSSION

Since the discovery of a minimum in the electrical resistivity versus temperature curve for gold at low temperatures by de Haas *et al.*,[6] quite extensive experimental and theoretical studies have been made on problems of this type. A recent review summarizes the salient aspects of these investigations.[7] For years it was thought that the low-temperature resistivity anomalies, which are usually accompanied by anomalous behavior in other physical properties, occur only in simple metals such as gold, silver, copper, and magnesium when

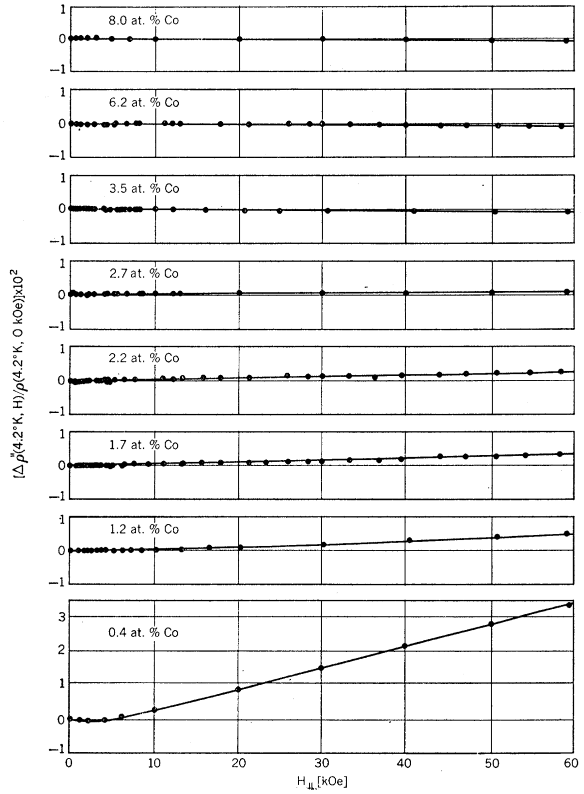

FIG. 6. Longitudinal relative electrical magnetoresistivity of chromium alloys at $T=4.2^\circ$K as a function of $H_{\parallel}$.

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contaminated with certain transition metals. Some recent studies[8–16] have clearly revealed that similar phenomena also exist in certain alloys where a transition metal is the solvent. In particular, electrical resistivity anomalies have been observed in titanium, zirconium, hafnium,[9,10,16] molybdenum,[11,12,15] and rhodium.[14]

Our electrical resistivity results, as presented in Figs. 1 and 2, clearly show that low-temperature minimum is produced in chromium by cobalt. Chromium is not only a transition metal but is also a more complicated element than, say, titanium or molybdenum since it exhibits a special form of collective electron antiferromagnetism. In fact, from 0 to 122°K, chromium possesses sinusoidal spin arrangements (linear spin density waves) with the wave vector of the modulation parallel to the spin polarization.[17] Above 122°K, according to recent studies,[18–20] the direction of the wave vector becomes perpendicular to the polarization direction with some preferred orientations. The appearance of the resistivity minimum in chromium-cobalt alloys is the first observed case of such behavior in a system where the solvent is a magnetically ordered substance. Thus, the existence of the electrical resistivity anomalies at low temperatures may be more widespread than previously realized.

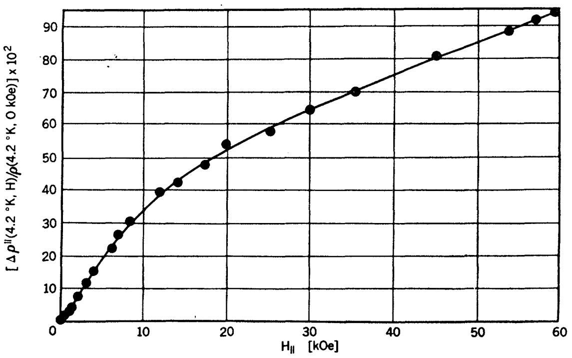

FIG. 7. Longitudinal relative electrical magnetoresistivity of chromium at $T=4.2$°K as a function of $H_{\|}$.

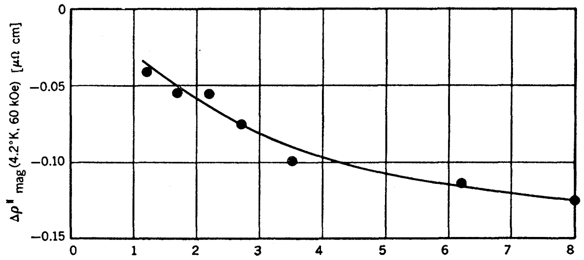

FIG. 8. Magnetic component of the longitudinal electrical magnetoresistivity of chromium-cobalt alloys at $T=4.2$°K in $H_{\|}=60$ kOe as a function of concentration.

Recently[21–34] there have been very active developments in theories of the electrical transport properties of magnetically dilute binary alloys. All these theories assume the existence of a localized magnetic moment on the impurity atom. For the purpose of discussion one may look at the most recent version[26] (more exact than the original one) of the Kondo theory which predicts that the electrical resistivity due to the *s*-*d* interaction in dilute alloys can be expressed as

$$\rho_{s-d}=\frac{\pi^3 S(S+1)c\hbar}{ze^2K_F}\left[\left(\ln\frac{T}{T_{\max}}\right)^2+(\tfrac{1}{2}\pi)^2\right]^{-1}, \qquad (1)$$

where S is the quantum number associated with the angular momentum $\mathbf{S}$ of an impurity atom, c the impurity concentration, $\hbar=h/2\pi$, h being the Planck constant, z the number of conduction electrons per atom, e the electronic charge, K_F the magnitude of the Fermi wave vector, and T the absolute temperature. The quantity $T_{\max}$ is defined by

$$kT_{\max}\approx E_F e^{1/2Jn}, \qquad (2)$$

where k is the Boltzmann's constant, E_F the Fermi energy, J the *s*-*d* exchange integral, and n the density of states for one direction of spin. Equation (1) may be used for either positive or negative values of J, contrary to the original form of the Kondo theory[24] which was physically realistic only for $J<0$. From Eq. (1) one can conclude that the *s*-*d* electrical resistivity term

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allows the formation of the resistivity maximum at $T_{\max}$, this temperature being independent of c. Furthermore, when $J<0$, $T_{\max}$ is usually so low that one observes increasing electrical resistivity with decreasing temperatures. On the other hand, when $J>0$, $T_{\max}$ is so high that decreasing temperatures give decreasing electrical resistivity. Equation (1) also implies that the resistivity at $T_{\max}$ is independent of J and the *s-d* resistivity contribution goes to zero as T decreases to zero.

The original version of the Kondo theory predicted that the *s-d* resistivity varies as $c \ln T$. This behavior, coupled together with a electron-phonon resistivity taken to be proportional to T^5, predicted that for $J<0$ the temperature $T_{\min}$ would increase as $c^{1/5}$. It should be noted that Eq. (1) reduces to a single $\ln T$ behavior only when $kT \ll D$, where D is a measure of the electronic band width. In other words, Eq. (1) can be expanded in terms of $\ln(T/T_0)$, where T_0 is an arbitrary temperature not too close to $T_{\max}$.

Although the temperature $T_{\min}$ for chromium-cobalt alloys becomes larger with higher cobalt concentration (Fig. 4), the initial increase is much more rapid than being proportional to $c^{1/5}$ or $c^{1/3}$ as expected from the simple Kondo theory. The $c^{1/3}$ dependence would be more appropriate for chromium alloys because for transition metals the electron-phonon electrical resistivity is closer to T^3 than T^5 behavior at low temperatures. The rapid increase of $T_{\min}$ with the cobalt concentration in chromium cobalt alloys is in sharp contrast with the behavior of $T_{\min}$ in dilute alloys of iron in gold[35] and in 80.0 at.% molybdenum -20.0 at.% niobium solid solution.[15] For these systems $c^{1/5}$ law appears to be obeyed. Furthermore, according to Sugawara,[36] yttrium-rich yttrium-cerium alloys at low temperatures exhibit minima in the electrical resistivity curves as predicted by the simple Kondo theory with $T_{\min}$ proportional to $c^{1/(4.1\pm 0.1)}$. On the other hand, similarly to our results for chromium-cobalt alloys, Cape and Hake[16] found that various localized magnetic impurities in titanium and hafnium produced effects which could not be described by the simple Kondo theory. Obviously, the detailed behavior of the electrical resistivity of a metal containing various types of impurities capable of producing resistivity minima is a more complicated phenomenon than previously realized. In the case of chromium, one should recall that this metal is magnetically ordered itself, and the possible effect of this state on the localized moment arrangements from the viewpoint of the transport properties has not been included in any of the abovementioned theories.

Now, let us look at the magnetoresistivity results. Just as with iron at low concentrations, when cobalt is added to chromium its large positive transverse total magnetoresistivity (at $H_{\perp}=12$ kOe) decreases rapidly, and for about 2 at.% cobalt content is about zero (Fig. 5). Further additions of cobalt seemingly have no significant effect. This behavior is very different from that found in chromium-iron alloys for which amounts of iron larger than 2 at.% cause very sizeable negative magnetoresistivity. The longitudinal total magnetoresistivity data (Fig. 6) for chromium-cobalt alloys are essentially similar to those for the transverse case.

Phenomenologically, the total electrical resistivity of a dilute binary alloy, whose solvent atoms possess localized magnetic moments, in the presence of, say, a longitudinal magnetic field of magnitude $H_{\parallel}$ at the temperature, T, can be written as

$$\rho(T,H_{\parallel})=\rho_0+\rho_p(T,H_{\parallel})+\rho_{\mathrm{mag}}(T,H_{\parallel}). \tag{3}$$

In Eq. (3), ρ_0 represents the electrical resistivity due to all nonmagnetic scattering potentials, $\rho_p(T,H_{\parallel})$ the resistivity of the pure solvent, and $\rho_{\mathrm{mag}}(T,H_{\parallel})$ the resistivity due to the localized magnetic moments on the solute atoms. The quantity of theoretical interest is the resistivity contribution $\rho_{\mathrm{mag}}(T,H_{\parallel})$. Because of the complications in the $\rho(T)$ versus T curves of chromium-cobalt alloys (Fig. 1) due to the antiferromagnetic paramagnetic transitions, we cannot obtain $\rho_{\mathrm{mag}}(T,H_{\parallel})$ for these alloys. However, the change in $\rho_{\mathrm{mag}}(T,H_{\parallel})$, defined by $\Delta\rho_{\mathrm{mag}}{}^{\parallel}(T,H)=\rho_{\mathrm{mag}}(T,H_{\parallel})-\rho_{\mathrm{mag}}(T,0)$, can be, in principle, easily obtainable from the experimental data. From a simple localized-moment viewpoint, one would expect $\Delta\rho_{\mathrm{mag}}{}^{\parallel}(T,H)$ to be negative and to increase with increasing magnetic fields until a saturation occurs. These features should result from the gradual ordering of the moments by the applied magnetic field. Because of the smallness of $\Delta\rho_{\mathrm{mag}}{}^{\parallel}(4.2°\mathrm{K},H)$ for the chromium-cobalt alloys, this quantity has been determined only at $H_{\parallel}=60$ kOe. The results are shown in Fig. 8, indicating that, indeed, the change in the magnetic component of the total electrical resistivity becomes negative in the chromium alloys containing more than 1 at.% cobalt.

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