

perature interval near $T_{c3}(H)$, in which the contribution of the surface fluctuations to the magnetization is more substantial. From (20), (21), (31), and (38) it is seen that this temperature interval should satisfy the condition

$$(T - T_{c3}(H))/T_{c3}(H) < \xi_0 l / R \lambda. \quad (39)$$

Here $\xi_0 = v_F / T_{c3}(H) \sim 10^{-4}$ cm. In the experiments of Ref. 7, $R \sim 0.1$ cm and $\lambda = (\rho H)^{-1/2} \sim 10^{-4}$ cm. If we put $l \sim 10^{-5}$ cm (the order of magnitude of the electron mean free path in the alloy Pb+4 at.% Tl), then the condition (39) is satisfied in the temperature interval $(T - T_{c3})/T_{c3} < 10^{-4}$, which agrees with experiment⁷ in order of magnitude (the data given in Ref. 7 for the surface-fluctuation diamagnetism are insufficient for a detailed comparison of our results with the experimental data).

In conclusion, the author thanks A. F. Andreev for a discussion of the results.

¹In Ref. 9 the author calculated the response of the system to an external perturbation that is a function of only the time coordinate. In the present case A_1 is a function of only the spatial coordinates.

¹J. P. Gollub, M. R. Beasley, and M. Tinkham, Phys. Rev. Lett. 25, 1646 (1970).

²A. Schmid, Phys. Rev. 180, 527 (1969).

³R. E. Prange, Phys. Rev. B 1, 2349 (1970).

⁴K. Maki and H. Takayma, J. Low Temp. Phys. 5, 313 (1971).

⁵J. Kurkijärvi, Y. Ambegoakar, and G. Eilenberger, Phys. Rev. B 5, 868 (1972).

⁶P. A. Lee and M. G. Payne, Phys. Rev. B 5, 923 (1972).

⁷J. P. Gollub, M. R. Beasley, R. Callarotti, and M. Tinkham, Phys. Rev. B 7, 3039 (1973).

⁸L. V. Keldysh, Zh. Eksp. Teor. Fiz. 47, 1515 (1964) [Sov. Phys. JETP 20, 1018 (1965)].

⁹O. D. Cheishvili, Zh. Eksp. Teor. Fiz. 66, 1862 (1974) [Sov. Phys. JETP 39, 916 (1974)].

¹⁰O. D. Cheishvili, Fiz. Nizk. Temp. 1, 177 (1975) [Sov. J. Low Temp. Phys. 1, 85 (1977)].

Translated by J. G. Adashko

Anomalous temperature dependence of resistance of doped beryllium

S. V. Varyukhin and V. S. Egorov

I. V. Kurchatov Institute of Atomic Energy, Academy of Sciences of the USSR, Moscow

(Submitted 17 July 1978)

Zh. Eksp. Teor. Fiz. 76, 597-606 (February 1979)

The resistance of four beryllium samples, differing greatly in respect of the residual mean free path of electrons and magnetic impurity concentration, was measured in the temperature range 2-70°K. All samples exhibited an increase in the resistance as a result of cooling with a minimum in the region between 10 and 17°K. The temperature dependences in a magnetic field were also determined. The observed anomalies were largely due to the influence of magnetic impurities.

PACS numbers: 72.15.Eb, 72.15.Lh

INTRODUCTION

We reported earlier¹ that the temperature dependence of the resistance of beryllium has a minimum and that the position of this minimum and its depth are in agreement with the theoretical estimates of Kozlov and Flerov.² The theoretically predicted anomalous temperature dependence² is due to the following reasons: at low temperatures in metals when the characteristic wavelength of thermal phonons becomes greater than the electron mean free path governed by the scattering on nonmagnetic impurities and defects, these two processes—i.e., the scattering by phonons and impurities—can no longer be regarded as independent and the phonon contribution to the resistance is no longer described by the usual Bloch-Grüneisen law $\rho \propto T^5$. The characteristic range of temperatures T where this law is replaced with a logarithmic temperature dependence of the resistance is defined by the relationships

$$T_2 \ll T \ll T_1; \quad T_1 = \frac{\Theta_D \hbar}{\tau \epsilon_F} \sim c \Theta_D, \quad T_2 = \frac{T_1 \Theta_D}{\epsilon_F}.$$

Here, Θ_D is the Debye temperature; \hbar is the Planck constant; τ is the collisional electron lifetime; ϵ_F is the Fermi energy; c is the concentration of impurities and defects. The effect under consideration is most likely to be exhibited by beryllium: the exceptionally high values of the Debye temperature $\Theta_D = 1416^\circ\text{K}$ (Ref. 3) and of the ratio Θ_D/ϵ_F (in the case of beryllium this ratio is anomalously large compared with other metals and $\epsilon_F = 0.7$ eV) make this range of temperatures not too narrow and convenient for measurements. For example, if $c \sim 1-2\%$, these temperatures are $\sim 10^\circ\text{K}$. Moreover, the ratio Θ_D/ϵ_F determines the absolute value of the effect.

On the other hand, it is known that in the case of metals at low temperatures the scattering by noninteracting magnetic impurities may give rise to a logarithmic temperature dependence of the resistance, first discovered for gold:^{4,5} this is known as the Kondo effect,⁶ which is responsible for the resistance minimum. The sample investigated by us earlier¹ contained a small amount ($\sim 10^{-2}\%$) of the iron impurity and this could also

increase the resistance at low temperatures because of the Kondo effect. In spite of the enormous number of theoretical and experimental investigations of this effect, the sources available to us (including reviews⁷⁻⁹) indicate that the Kondo effect has not yet been investigated in beryllium and, moreover, there is even one negative result¹⁰ in which the nickel impurity did not give rise to this effect. Therefore, the question of a possible influence of magnetic impurities on the resistance of beryllium would seem to be of intrinsic interest.

The results obtained for a single sample were insufficient to determine reliably the nature of the temperature anomaly¹ even when measurements were carried out in longitudinal and transverse magnetic fields. Therefore, it seemed extremely desirable to investigate similar temperature dependences of the resistance of beryllium samples with different concentrations of magnetic impurities and different values of the residual resistance. The results of such measurements are given below: they were carried out on beryllium samples available to us and these had different impurity compositions and different electron mean free paths; moreover, the precision with which the temperature was measured was somewhat higher than in our earlier work.¹

EXPERIMENTS

The principal properties of the investigated four samples are collected in Table I. Here, the quantity $\alpha = (\rho_{300} - \rho_{4.2})/\rho_{4.2}$ is inversely proportional to the residual resistance, which is governed by the total number of impurities and defects in a crystal. The composition of the principal impurities dominating the residual resistance is generally unimportant in the experiments of the kind described below. Table I gives the results of an analysis of the content of the principal magnetic impurities, which can give rise to the Kondo effect. The analysis was carried out by emission spectroscopy and was accurate to within ~30%. Samples 1, 2, and 4 were single crystals, whereas sample 3 was polycrystalline.

The sample mounting procedure was the same in all cases. A thin (~0.2–0.3 mm) plate was cut from the original ingot in such a way that its plane coincided with the basal plane of the crystal. This was necessary because of brittleness of beryllium, which cleaved along the basal plane. Next, the plates were ground down to a thickness slightly less than 0.1 mm and cut into "serpentine" samples¹⁾ by spark machining (this was done also for sample 3 which was cut from a polycrystalline ingot). In their final shape, samples 1–4 had room-temperature resistances R of 0.23, 0.32, 0.37, and 0.05 Ω . Next, each sample was bonded by a thin layer of wax or BF-2 adhesive to the same ingot from which it was cut so as

to minimize possible stresses during cooling. The dimensions of the ingots were $2 \times (5-10) \times 25$ mm. The width of our samples was 0.25–0.4 mm and the length of each section of the serpentine was an order of magnitude greater than the width, i.e., 5–10 mm (this made it possible to assume that the magnetic field directed along the cuts was basically longitudinal relative to the current).

The current and potential contacts were beryllium bronze springs 0.2 mm in diameter. Thermometers were attached directly to the ingot: a junction of a copper-constantan thermocouple and an Allen-Bradley thermometer were attached with the aid of BF-2, and a TSG-2 resistance thermometer (made at All-Union Scientific-Research Institute of Physicotechnical and Radio Engineering Measurements, Moscow) was bonded with Wood's alloy. The ingot and the thermometers were placed inside a copper can fitted with a heater. The temperature of the ingot could be varied over a very wide range by altering the heating power and the pressure of the heat-exchange medium (helium). The temperature of the sample and ingot could be regarded as equal within the limits of the necessary precision. The temperature rise due to the passage of a measuring current of ~200 mA was only ~0.1 K at $T < 4.2$ K, which was demonstrated clearly by a comparison of the results of measurements on a liquid and a gas, and also those carried out using various currents; at higher temperatures the heating effect could only be less.

The temperature of the sample was measured with the TSG-2 thermometer in the range 2–3 K to within ± 0.05 K. Its calibration below 4 K was checked against the saturated helium vapor pressure. Above 30 K, we used the thermocouple, which was calibrated with the aid of TSG-2 and against the boiling point of pure nitrogen. In magnetic fields the temperature was determined with the Allen-Bradley thermometer, whose magneto-resistance was allowed for. The total error in the temperature measurement throughout the range from 2 to 70 K did not exceed ± 0.2 K. The resistance was measured by the four-contact method using an R-348 potentiometer and the precision of these measurements was 2×10^{-5} .

RESULTS OF MEASUREMENTS

The temperature dependences of the resistance are plotted in Fig. 1. The ordinate gives the resistance of a sample reduced to the phonon component at room temperature: $\rho(T) = R(T)/[R(300) - R(4.2)]$, i.e., the dimensionless quantity closest to the resistivity, whose direct measurements would have resulted in much greater errors because of the irregular shape of the samples. The numbers of the curves in Fig. 1 are the same as the numbers of samples in Table I. Curve 2 represents the results obtained in Ref. 1. Since the amounts of impurities (including the magnetic impurities) were lowest in sample 1, we may assume that the impurity component of the temperature dependence of the resistance of this sample is minimal and the phonon part of the resistance is approximated satisfactorily by the $\rho \propto T^{3.7 \pm 0.2}$ law in a wide range of temperatures (the $\rho \propto T^5$ law is not observed). It is clear from Fig. 1 that all the dependences can be represented conveniently by

TABLE I.

Sample No.	α	Impurities, 10^{-3} at. %						
		Fe	Ni	Mn	Tl	V	Cr	Co
1	61	1.3	0.65	0.1	<3	<1	<1	<1
2	10.5	10	1.6	0.9	<3	<1	<1	<1
3*	1.6	14	9	1.3	20	20	<1	<1
4	1.1	6	2.2	0.38	8	20	<1	<1

*Polycrystalline sample; the others were single crystals.

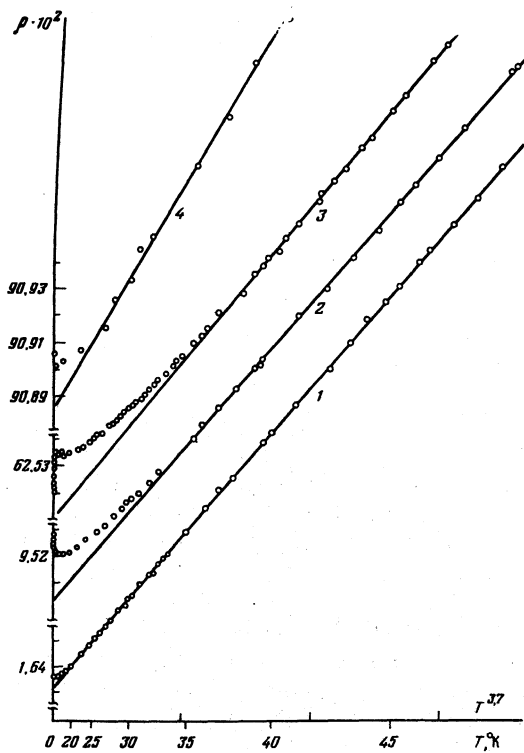


FIG. 1. Temperature dependences of the resistance. The numbers of the curves are labeled in the same way as the samples. The lines are drawn in accordance with the $\rho \propto T^{3.7}$ law. The scale is the same for all the dependences but the resistances at absolute zero are displaced, for convenience, by $\sim \rho_0$.

$$\rho(T) = \rho_0 + AT^{3.7} + \rho_{im}(T),$$

where $\rho_{im}(T)$ is the correction to the resistance due to the presence of impurities. For the first three samples the constant A is the same, but for sample 4 it is slightly higher. This is probably due to the fact that the main impurity in this sample was copper, whereas in the others it was oxygen.

Figure 2 shows parts of the dependences $\rho(T)$ plotted on a linear temperature scale at $T < 30$ K. The numbers of the curves correspond to the numbers of the samples, exactly as in Fig. 1. The scale is the same for all the curves.

It is clear from these results that the temperature dependences of the resistance of all the samples are anomalous because of the rise as a result of cooling, which is responsible for the minimum of $\rho(T)$. The position of the minimum shifts slowly from one curve to another in the temperature range 10–17 K. Moreover, sample 3 (the lowest curve in Fig. 2) exhibits another fall of the resistance below 10 K and this gives rise to a second minimum.

A comparison of the results obtained for the various samples differing in respect of ρ_0 (i.e., in respect of the mean free path of electrons) by a factor of almost 60 shows no correlation in the observed anomalies of $\rho(T)$ which might be related to the theory of Ref. 2, where the main variable parameter is ρ_0 . In fact, the correction

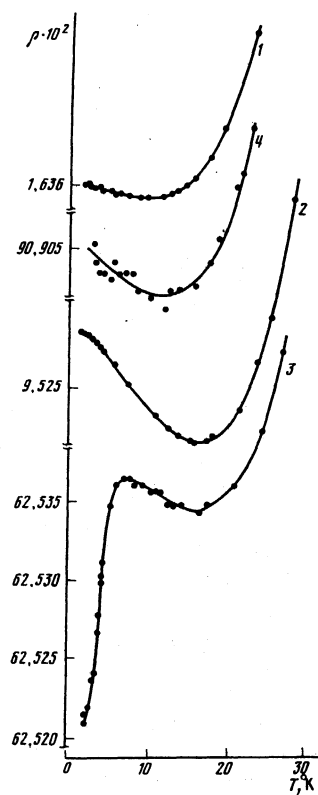


FIG. 2. Dependences $\rho(T)$ at low temperatures plotted on a linear temperature scale. The positions of the curves from top to bottom correspond to increasing order in the magnetic impurity concentration.

$\rho_{im}(T)$ is approximately the same for all the samples in the investigated temperature range although $T_1 \sim c\Theta_D$ varies (as pointed out above) by more than one order of magnitude. Moreover, the absolute value of $\rho_{im}(T)$ is not correlated with the residual resistance: the value of ρ_{im} for sample 4 is less than for sample 2, although the residual resistance of the former is an order of magnitude higher than that of the latter. This appears particularly clearly when a comparison is made of the dependences $\rho(T)$ of samples 1 and 2 (Fig. 3), which differ most in respect of the magnetic impurity content. Hence, we may conclude that the influence of the magnetic impurities predominates in the observed effect.

It follows from Table I that the number of magnetic impurities in all the samples is small (compared with the total number of impurities), which suggests an in-

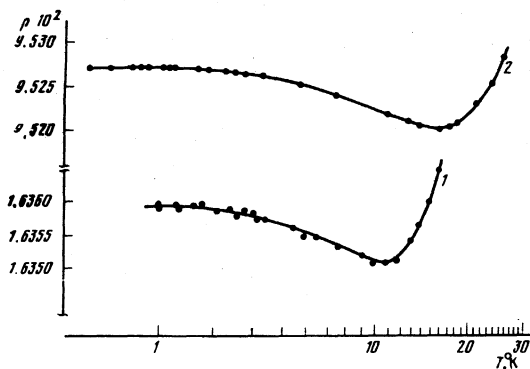


FIG. 3. Dependences $\rho(T)$ plotted on a logarithmic temperature scale for the "purest" samples 1 and 2. The ordinate scale of sample 1 is magnified by a factor of 7.5.

crease in the resistance because of the Kondo effect. In this case^{9,9} the correction to the resistance $\rho_{im}(T)$ associated with the scattering by magnetic impurities rises logarithmically as a result of cooling in the range $T \sim T_K$, where T_K is the Kondo temperature.^{9,11} The absolute value of ρ_{im} increases with the magnetic impurity concentration. If the curves are arranged in the order of increasing ρ_{im} , as in Fig. 2—which is identical with the standard dependences $\rho(T)$ of the samples exhibiting the Kondo effect and arranged so that the amount of the magnetic impurities increases in the downward direction (see, for example, Fig. 3 in Ref. 8 for the Kondo effect of manganese atoms in a silver matrix), it is found that the sequence of samples 1, 4, 2, and 3 corresponds approximately to the increase in the concentrations of the iron and manganese impurity atoms, which is approximately proportional to the depth of the minimum; it should be noted that the amount of iron is in almost all cases an order of magnitude greater than the amount of manganese (Table I). We can therefore make the preliminary assumption that the main contribution to $\rho_{im}(T)$ is made by the magnetic iron and manganese atoms.

The phonon part and the logarithmic correction $\rho_{im}(T)$ should give rise to a minimum in the temperature dependence of the resistance and the position of this minimum should vary weakly with the magnetic impurity concentration: $T_{min} \propto c^{1/n}$, where n is the power exponent of the temperature dependence of the phonon part of the resistance (for the Bloch law we usually have $\rho \propto T^5$ and $n=5$). In the sequence of curves 1, 4, 2, and 3 in Fig. 2 (this is also clear in Fig. 3), the position of the minimum varies from 10 to 17°K, and in the same range the concentration of the iron (and manganese) atoms increases by a factor of almost 10 (see Table I). This is in satisfactory agreement (within the limits of the experimental error in the determination of the temperature of the minimum T_{min} and the impurity concentration) with the expected dependence $T_{min} \propto c^{1/3.7}$.

On increase in the magnetic impurity concentration the interaction between the nearest atoms becomes stronger and cooling results in short-range magnetic ordering (spin glass) suppressing the resistance ρ_{im} , as found for sample 3.

The results obtained can be used to find the Kondo temperature T_K , which is defined as the midpoint of the linear part of the temperature dependence of the Kondo correction $\rho_{im}(T)$ plotted in the coordinates ρ_{im} and $\log T$ (Refs. 9 and 11). The temperature-dependent correction $\rho_{im}(T)$ can be separated with satisfactory accuracy for samples 1, 2, and 3 because—as pointed out above—this correction is small for sample 1 and the constant A is the same for all three samples. Hence, it also follows that the residual (nonmagnetic) impurities in these samples make no significant contribution to the phonon spectrum and the correction $\rho_{im}(T)$ is governed entirely by the magnetic impurities. Figure 4 shows, on a logarithmic temperature scale, the corrections $\rho_{im}(T)$ obtained in this way. If we replot these dependences with $\rho_{im}(T)/c_m$ as the ordinate (c_m is the concentration of the magnetic impurity), we should obtain a universal curve,^{9,11} which is in approximate agreement with the obtained re-

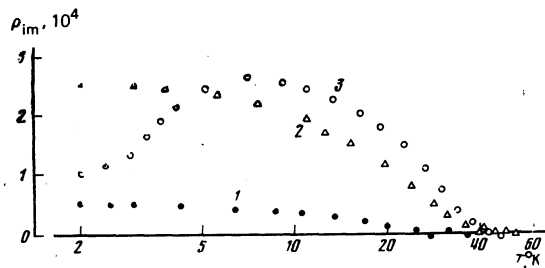


FIG. 4. Dependences $\rho_{im}(T)$ on a logarithmic temperature scale. The points are labeled in the same way as the samples.

sults. However, we can only assume that the main contribution is due to the iron and manganese impurities and, therefore, the exact value of c_m is not known. Nevertheless, the results obtained give the value of T_K with satisfactory accuracy: we can see from Fig. 4 that this value lies in the range 20–30°K.

MEASUREMENTS IN MAGNETIC FIELDS

We also investigated the influence of a magnetic field on the resistance of samples at various temperatures. The measurements were carried out in transverse and “longitudinal” mutual orientations of the magnetic field and current in the sample. The longitudinal orientation corresponded to the direction of the magnetic field parallel to a long section of the serpentine (in this case a small part of the sample was in a transverse magnetic

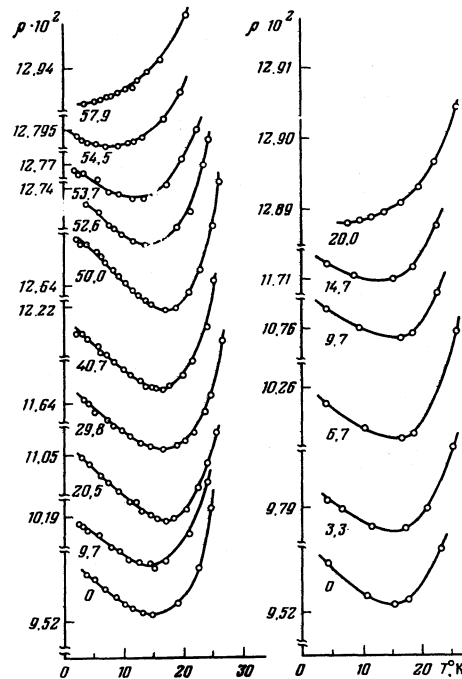


FIG. 5. Dependences $\rho^H(T)$ for sample 2. The ordinate scale is the same for all the curves but the values of the resistance at absolute zero are displaced. The numbers alongside each curve give the magnetic field in kilooersted; the left part of the figure gives curves obtained in longitudinal magnetic fields and the right part those obtained in transverse fields (the magnetic field was always applied in the basal plane of the crystal).

field).

The magnetic-field dependences of the resistance $\rho^T(H)$ of all four samples were nearly quadratic. Figure 5 shows the temperature dependence $\rho^H(T)$ obtained in longitudinal and transverse fields for sample 2. Similar dependences for sample 3 are plotted in Fig. 6. The differences between the influence of the longitudinal and transverse fields are in the latter case so small that only one figure is given. No clear changes in the anomalous behavior $\rho^H(T)$ could be observed for the other two samples. In the case of sample 1 the dominant contribution to $\rho^H(T)$ in the longitudinal orientation was due to the change in the magnetoresistance: only the fall of the resistance on increase in temperature was observed. (For this sample the Larmor radius became of the order of the mean free path of electrons in a magnetic field of ~ 8 kOe.) For sample 4, the magnitude of the effect (depth of the minimum) in a magnetic field became of the same order as the experimental error and the latter increased somewhat because of the magnetic field instability.

It is clear from these results that the application of a magnetic field destroys the anomalous correction ρ_{im} and that in the case of sample 3 this is observed in magnetic fields of ~ 5 kOe. In the case of sample 2 with a lower concentration of magnetic impurities the minimum disappears in a much weaker magnetic field. This is generally in qualitative agreement with the current ideas on the ordering influence of a magnetic field on the spins of impurity atoms, which destroys the additional resistance; however, it should be pointed out that some of the observations are difficult to explain on the basis of the Kondo effect. For example, in the case of sample 2 (Fig. 5) the depth of the minimum changes in different ways in longitudinal and transverse magnetic fields, and in the case of sample 3 (Fig. 6), an increase in the magnetic field has a greater influence on the maximum of $\rho(T)$ than on its position.

CONCLUSIONS

It follows from the above results that the anomalous temperature dependence of the resistance of beryllium, i.e., the deviation of $\rho(T)$ from the Matthiessen rule because of the presence of impurities, cannot be explained on the basis of the theory of Kozlov and Flerov,² contrary to the earlier conclusion.¹ We must admit that, unfortunately, all the samples had magnetic impurities and although their number was much less than the numbers of the other defects, the whole or most of the effect was due to these impurities. Even in the case of sample 4 with the lowest concentration of the magnetic impurities (compared with the other samples) the value of ρ_{im} was governed only by the magnetic impurities and the other impurities simply resulted in a steeper temperature rise of the resistance (and, clearly, of ρ_0).

It follows that with the exception of some features manifested in the effects of magnetic fields, the observed

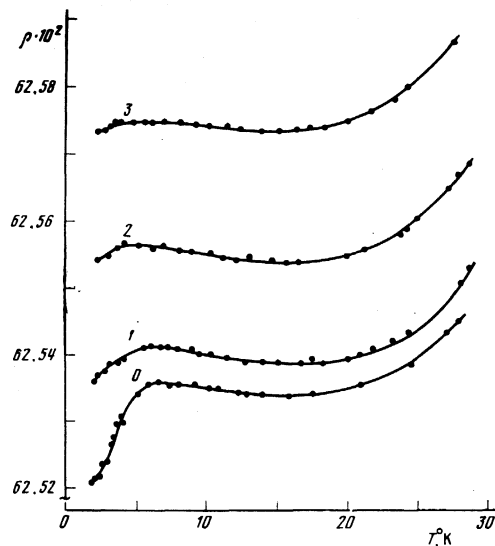


FIG. 6. Same as Fig. 5 but for sample 3. The magnetic field was longitudinal (the dependence in a transverse field were the same except for the much greater shift due to magnetoresistance).

anomalies of the dependences $\rho(T)$ can be described satisfactorily by the theory of the Kondo effect. We may assume that the absence of a significant contribution to $\rho_{im}(T)$, in conflict with the theoretical predictions of Kozlov and Flerov,² is due to the high value of the parameter Θ_D/ϵ_F , which—on the one hand—should give rise to a considerable magnitude of the expected effect in beryllium and—on the other—reduce the temperature interval between T_1 and T_2 ; the latter effect may be more important.

The authors are grateful to N. A. Chernoplekov for his interest and encouragement.

¹We take this opportunity to thank Yu. P. Gaïdukov for facilities to carry out this operation.

¹V. S. Egorov and S. V. Varyukhin, Pis'ma Zh. Eksp. Teor. Fiz. 25, 58 (1977) [JETP Lett. 25, 52 (1977)].

²A. N. Kozlov and V. N. Flerov, Pis'ma Zh. Eksp. Teor. Fiz. 25, 54 (1977) [JETP Lett. 25, 49 (1977)].

³G. Ahlers, Phys. Rev. 145, 419 (1966).

⁴A. J. Croft, E. A. Faulkner, J. Hatton, and E. F. W. Seymour, Philos. Mag. 44, 289 (1953).

⁵Yu. P. Gaïdukov, Zh. Eksp. Teor. Fiz. 34, 836 (1958) [Sov. Phys. JETP 7, 577 (1958)].

⁶J. Kondo, Solid State Phys. 23, 183 (1969).

⁷G. J. van den Berg, Prog. Low Temp. Phys. 4, 194 (1964).

⁸M. D. Daybell and W. A. Steyert, Rev. Mod. Phys. 40, 380 (1968).

⁹G. Grüner and A. Zawadowski, Rep. Prog. Phys. 37, 1497 (1974).

¹⁰A. P. Klein and A. J. Heeger, Phys. Rev. 144, 458 (1966).

¹¹J. S. Schilling, P. J. Ford, U. Larsen, and J. A. Mydosh, Phys. Rev. B 14, 4368 (1976).

Translated by A. Tybulewicz