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CERTAIN PHYSICAL PROPERTIES OF COBALT AND NICKEL BORIDES

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Translation of "Nekotoryye fizicheskiye svoystva boridov kobal'ta i nikelya", Fizika metallov i metallovedeniye, vol. 33, (April), 1972, pp 773-780

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16. Abstract
Study of the temperature dependence of the electrical resistivity, the thermal conductivity and the thermal emf of cobalt and nickel borides. In the case of the nickel borides the magnetic susceptibility and the Hall coefficient were determined at room temperature. The results obtained are discussed with allowance for the current carrier concentration, the effect of various mechanisms of current-carrier scattering and the location of the Fermi level relative to the 3d band.

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Translation of "Nekotoryye fizicheskiye svoystva boridov kobal'ta i nikelya," Fizika metallov i metallovedeniye, Vol. 33, (April), 1972, pp. 773-780.

The temperature dependence of specific electrical resistance ρ, coefficients of heat conductivity λ and thermal emf α of cobalt and nickel borides was studied in the interval 100 - 1200°K. Magnetic susceptibility χ and the Hall coefficient R were determined for nickel borides at room temperature. The findings are discussed with regard for the concentration of current carriers, action of different mechanisms for their scattering, and the location of the Fermi level in relation to the 3d-zone.

CERTAIN PHYSICAL PROPERTIES OF COBALT AND NICKEL BORIDES

I. I. Kostetskiy and S. N. L'vov*

Despite the great practical importance of cobalt and nickel borides /773** [1], their physical nature has not been sufficiently studied. In a theoretical respect, these compounds are important both from the viewpoint of crystal chemistry, since three types of bonds are often simultaneously realized in them, Me-Me, Me-B and B-B, and also because of the presence of magnetic transformations in them.

Cobalt forms three compounds with boron: Co_3B, Co_2B and CoB [2]. The existence of nickel borides has been established the most reliably: Ni_3B, Ni_2B and NiB [3]. Co_3B and Co_2B borides are known as ferromagnetic. Ni_3B and Ni_2B belong to paramagnetics, while NiB and CoB apparently are diamagnetics. There are very few published data on the physical properties of the indicated compounds, and they are often contradictory. Only their magnetic characteristics have been studied more or less completely [2,4-6] and their x-ray absorption spectra [7]. The obtained results permit certain conclusions to be drawn regarding the electron structure of the examined compounds. However, as yet there have not been any studies of their kinetic phenomena. For this reason, this work defined ρ, λ and α at 100-1200°K for all the aforementioned borides, and also measured R and χ at room temperature for nonferromagnetic borides. The findings are discussed from the viewpoint of the effect of different scattering mechanisms on the process of charge transfer, their concentration and the location of the Fermi level in relation to the 3d-zone.

The borides were obtained by the method of direct synthesis at the appropriate temperatures from electrolytic cobalt (99.7%), nickel (99.8%) and crystalline boron (99.5%). Test specimens were prepared according to the technique presented in [8]. X-ray and metallophysical analyses showed the one-phase nature of the test specimens, and chemical analysis showed the proximity of their composition to the stoichiometric.

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**Numbers in margin indicate pagination in original foreign text.

Despite the great practical importance of cobalt and nickel /1
borides [1]

The measurements were made according to the methods described in [9, 10].

Results of Experiment and Their Discussion

Table 1 presents data on all studied parameters at room temperature. Figures 1 and 2 show the temperature relationships ρ, λ and α. For CoB these relationships are given in table 2. As is apparent, compounds Co_3B, Co_2B, Ni_3B, Ni_2B and NiB have a metal nature of conductance, while CoB has a semiconductor nature. This requires separate examination of it. Therefore we will not discuss the properties of CoB in this work.

We will first examine the ferromagnetic borides Co_3B and Co_2B. /7

1. The relationship $\rho(T)$ of these compounds is typical for ferromagnetic metals: their electrical resistance rises with an increase in temperature, and in the transition through Curie point (747° for Co_3B and 429° for Co_2B [2]) the inclination of the $\rho(T)$ curve is diminished (see fig. 1). For the first of them, ρ is somewhat greater than for the second in the entire temperature interval.

As is known, electrical resistance of ferromagnetic metals consists of a number of terms governed by different mechanisms of current carrier scattering and by the change in their energy spectrum which is caused by the presence of a magnetic order [8]. Each of these terms naturally has an inverse dependence on the concentration of conductance electrons. As subsequent analysis shows, the correlation between the quantities of resistances of Co_3B and Co_2B is apparently also governed by the indicated dependence. In fact, evaluation of the concentrations of conductance electrons for the examined borides follows from the distribution of electrons by energy zones which can be obtained after using the data on saturation magnetization (1.116 and 0.764 μ_B per atom of Co in Co_3B and Co_2B [2]) and the Polingovskiy considerations about the number of B-B bonds. In examining the kinetic effects, it is expedient to pass from atomic distributions by zones to volumetric [8]. By assuming according to [7] that the straight bonds B-B, at least in Co_3B, are missing, we obtain in conversion for 1 cm^3 for Co_3B and Co_2B respectively:

$$(3d)^{\sim 69,8}(4sp)^{\sim 8,6};\ (2sp)^{\sim 2,3}(3d)^{\sim 69,7}(4sp)^{\sim 7,8}. \quad (1)$$

TABLE 1. PHYSICAL PROPERTIES OF COBALT AND NICKEL BORIDES (200°K)

Compound	$\chi \times 10^6$ un. CGSM/g	$\chi \times 10^6$ un. CGSM/g x atom Me	$Rx10^4$ cm^3/C	$\rho x10^6$ Ohm x cm	$\alpha x10^6$ V/deg	λ, W/cm x deg
Co_3B	Ferrom.	—	—	50	—40	0,17
Co_2B	Ferrom.	—	—	65	—27	0,14
CoB	—0,27 (—0,3[6])*	—18,8	—104	1080	—51	0,17
Ni_3B	+1,41	+88	0	21 (25,5 [22])	—10,8	0,42
Ni_2B	+0,73 (+0,67 [6])	+47	+0,53	14	—1,6	0,55
NiB	—0,08 (—0,04 [6])	—5,5	+0,63	50	+2,3 (+3,0[5])	0,22

*The available published data are presented in the parentheses.

TABLE 2. TEMPERATURE RELATIONSHIP ρ, α AND λ FOR CoB

T, °K	$\rho x10^6$ Ohm x cm	$\alpha x10^6$ V/deg	λ W/cm x deg
100	1120	—40	0,20
200	1210	—46	0,18
300	1070	—51	0,17
400	960	—51	0,17
500	900	—56	0,16
600	850	—58	0,16
700	780	—57	0,16
800	710	—54	0,16
900	610	—48	0,16
1000	550	—42	0,16

In these distributions, the numbers over the symbols of the zones should be multiplied by 10^{22}, and then the number of corresponding electrons in 1 cm^3 is obtained. As is apparent from (1), the concentrations of 4sp-electrons in Co_3B is greater than in Co_2B. This is apparently explained by the lower resistance of the first boride than the second. /776

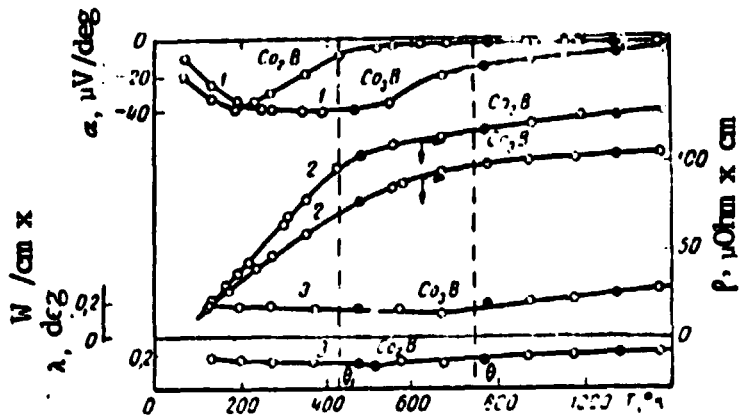

Figure 1. Temperature Relationship of Coefficients of Thermal emf α (1), Specific Electrical Resistance ρ (2) and Heat Conductivity λ (3) of Ferromagnetic Cobalt Borides

O--heating; ●--cooling; 0 and 0_1--Curie points for Co_3B and Co_2B respectively [2].

2. The absolute coefficient of thermal emf α for the examined borides has a negative sign, and with convergence to the Curie point it diminishes sharply in size (see fig. 1). In the paramagnetic region, it is comparatively small and maintains an almost constant value. The observed temperature relationship is qualitatively placed in the framework of the theoretical concepts developed for ferromagnetic metals. In works [12, 13], the following approximate formula was obtained for α

$$\alpha = -\frac{\pi^2 k^2}{e} T \left(\frac{3}{2\zeta} - \frac{N'}{N} \right), \qquad (2)$$

where ζ--Fermi level at temperature T; N and N'--density of states and its derivative for energy at the Fermi level in the unfilled d-subzone; *e*--charge of the current carriers with their sign. The second subzone is completely filled at low temperature.

Based on expression (2), the negative sign and rise in absolute quantity α with an increase in T in the region of low temperatures can be explained after assuming that in this case, ζ for both borides is located in the region of the minimum of the curve of state density ($N' \approx 0$), and that electron conductance is the dominant. With a further increase in temperature, as the Curie point is approached, there is

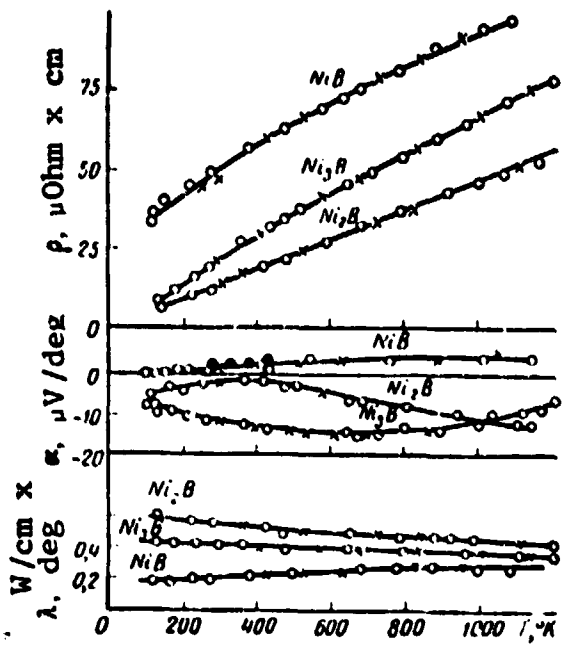

Figure 2. Temperature Relationship of Specific Electrical Resistance ρ, Coefficients of Thermal emf α and Thermal Conductivity λ of Nickel Borides

O--heating; X--cooling; ●--data of [5].

a rapid superposition of the d-subzones and the quantity ζ is shifted in relation to the curve of density of states of the previously unfilled d-subzone on the section of this curve with rising positive derivative. This causes a drastic decrease in $|\alpha|$ for both borides. After the Curie point, both d-subzones have already been completely superposed, and with a further rise in temperature, the superposition of ζ stops: α ceases to change drastically, which is actually observed. Analysis of the temperature course of α in direct proximity to the Curie point is complicated because of the effect of the second d-subzone.

3. With regard for formula (1) one can compute for Co_3B and Co_2B the degree of unfilling of the d-zone. The whole number of states in it in conversion for 1 cm^3 correspondingly equals 78.4 and 75.8 x 10^{22}, while the number of free d-states is 8.6 and 6.1 x 10^{22}. Then the relative degree of unfilling of the d-zones will be 10 and 8%, that is

roughly the same. By then using data on electron thermal capacity (γ = 7.05 and 6.70 $\mu J/deg^2$ x g x atom Me for Co_3B and Co_2B respectively. [11]), one can obtain the corresponding values of density of states on the Fermi level in conversion for 1 cm^3: 23.3 and 21.4 x 10^{22} le/ eV/cm^3. Since the density of the states which mainly have d-symmetry, are close among themselves on the Fermi level, the actual levels for both compounds pass in the region of the minimum, and their heights, judging from the close values α at low temperatures, are also roughly the same, one can conclude that the structure of the d-zone for both compounds near the Fermi level and above it is approximately the same. This conclusion agrees with the ideas of the model of the rigid band and coincides with the analogous conclusion in [7] for the lowest borides.

4. According to the obtained data (see fig. 1), the coefficient of heat conductivity of Co_3B and Co_2B in the region of the Curie point has a minimum which is characteristic for ferromagnetics [14-16]. In the ferromagnetic region where the most rapid growth of electrical resistance is observed with an increase in temperature, heat conductivity diminishes, and after the transition through the Curie point where the rate of its growth noticeably diminishes, the heat conductivity rises. A similar correlation of temperature relationships ρ /777 and λ is in qualitative correspondence to the requirements of the Wiedemann-Franz law. It, in turn, indicates the dominant role of the electron component in the process of heat transfer for both compounds.

5. We will now examine the nonferromagnetic borides Ni_3B, Ni_2B and NiB. The first two borides, according to [2, 17], reveal paramagnetism, while the latter is a diamagnetic. This agrees with the results of [6] (see table 1).

The susceptibility χ for Ni_3B and Ni_2B in calculation for 1 g x atom of metal (see table 1) has the same order as for the d-transitional metals. One can therefore assume that a considerable contribution is made by Pauli paramagnetism.[1] In this case χ must be in direct dependence on the density of states on Fermi level ζ. Then the high values of χ force us to assume the presence for them of an unfilled d-zone despite the small number of vacant places in the

[1]This hypothesis was confirmed by the studies we made on the temperature relationship of magnetic susceptibility of Ni_3B and Ni_2B.

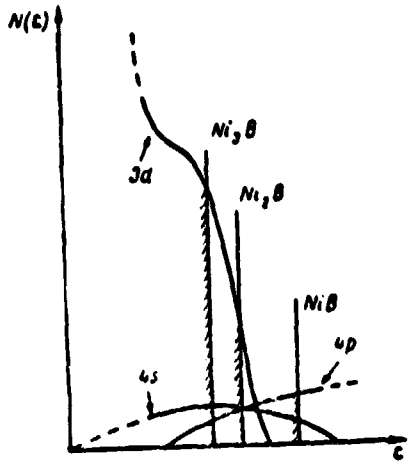

Figure 3. Suggested Mutual Arrangement of 3d-, 4s-, 4p-Zones and Fermi Levels for Nickel Borides.

3d-states of the metal nickel (0.6 per atom) and the donor role of boron [6] in the formation of borides. The Fermi level evidently passes through the right extreme steep slope of the curve N(ε) for the indicated borides where the density of states is still fairly great (fig. 3). For Ni_2B it must be located more to the right than for Ni_3B. In the case of NiB ($\chi < 0$), the quantity ζ is already located beyond the limits of the d-zone.

6. The conclusions drawn regarding the arrangement of ζ in relation to the 3d-zone agree with the observed changes in electrical resistance in the series Ni_3B, Ni_2B, NiB. In the entire temperature region ρ for Ni_2B is smaller than for Ni_3B, but with a transition to NiB it again increases. In order to explain the reasons for the change in ρ, one should evaluate how the concentration of the main current carriers (4sp-electrons) changes in the indicated series of borides, and take into consideration the effectiveness of the main mechanism for their scattering. Assuming, as in [17], that for different borides of one metal, the population density of the 4sp-states (γ_{sp} el/atom) is approximately the same, that is, that through the boron electrons mainly the d-states alone are filled, one can evaluate the change in concentration of 4sp-electrons in the examined series of borides if structural data are used to determine

the number of nickel atoms in a unit of volume of these compounds. As a result, we obtaind for the indicated concentrations, 7.93, 7.55 and 6.23 γ_{sp} x 10^{22} $1/cm^3$ respectively. The difference in concentrations of the actual current carriers from these 4sp-electrons is apparently still greater, since a certain portion of them are diverted for participation in the Ni-B bonds. This portion rises with an increase in the boron content. This diversion is responsible for the special /778 reduction in concentration of current carriers for NiB. However, in the transition from Ni_3B to Ni_2B, despite a certain reduction in carrier concentration, the electrical resistance, on the contrary, diminishes. This can be explained by weakening of their scattering.

As a consequence of the unfilling of the d-zone for Ni_3B and Ni_2B, the main contribution to electrical resistance is dictated by the scattering of the current carriers into d-states, and apparently, the reduced value of ρ of Ni_2B is associated with the lower value for it of $N_d(\zeta)$. The relatively high electrical resistance of NiB which is observed despite its lack of scattering into the d-zone, evidently can be induced by the significantly reduced concentration of current carriers. In addition, as is apparent from fig. 2, the studied test specimens of this compound have fairly high residual resistance.

7. Judging from the sign and relatively small size of the Hall coefficient R, besides the electrons, vacancies also participate in the conductance of the examined borides. This indicates the presence in these borides of at least two overlapping zones. These zones which provide the main contribution to conductance are the 4s- and 4p-zones.[2] It is natural to hypothesize that the zone which provides the vacancy contribution to conductance and is more than half filled is the 4s located more deeply as compared to the 4p-zone. The zone that is responsible for the electron contribution is the relatively elevated, slightly filled 4p-zone. In light of these considerations one should think that the population density of the sp-states which we designated above as ν_{sp} is very high in nickel borides. In any case, it is greater than one electron per atom of nickel. This means that in the 3-d zone of borides after distribution of the 10sp-electrons of nickel, considerably more free places remain for the boron electrons

[2]The contribution of the d-zone to conductance is small because of the low velocity of its electrons on the Fermi level.

than 0.6 per atom of nickel as is usually believed for the metal nickel. In this respect, yet another substantiation appears for the hypothesis that distribution of electrons for nickel of the type $3d^{9.4}4sp^{0.6}$ based on a very elementary calculation, is not quite correct.[3]. It apparently is closer to the distribution in atomic nickel. This conclusion facilitates the explanation of fairly strong paramagnetism observed in Ni_3B and Ni_2B since it becomes more understandable why free places still remain in the d-zone, despite the transition of boron electrons into the d-states in the formation of borides.

8. The coefficient of thermal emf α of nickel borides (see table 1, fig. 2) with an increase in the boron content rises, and for the NiB compounds changes sign from negative to positive. For Ni_3B and Ni_2B the relationship $\alpha(T)$ has a fairly complex appearance, while for Ni_3B and Ni_2B it is close to linear. The observed nature of the relationship $\alpha(T)$ is qualitatively explained in the framework of the hypotheses made by the arrangement of the Fermi level in relation to the 3d-zone.

Since the Fermi level for Ni_3B and Ni_2B passes in the d-zone, and therefore scattering of the current carriers is possible into this zone, the relationship $\alpha(T)$ can be expressed by formula (2). In analyzing this expression, we wil only take into account the electrons. A similar result is obtained for the vacancies.

For Ni_3B in a broad temperature interval, with a rise in temperature, α at first increases, and then smoothly diminishes, maintaining a negative sign. Because the Fermi level for the examined boride passes thorugh the right, fairly steep incline of the curve, $N(\varepsilon)$, the quantity $N'(\varepsilon)$, and consequently $\alpha < 0$ are in correspondence with the experiment. Since $N(\varepsilon)$ on the slope of the curve drastically depends on the energy, even a slight reduction in ζ caused by a rise in temperature, can significantly affect the nature of the relationship $\alpha(T)$ [20]. It is possible that as it drops, the Fermi level passes from the section of the curve $N(\varepsilon)$ with constant great slope to the section with diminishing slope [8] (see fig. 3). Then the

[3]The indicated distribution is currently criticized, on the basis of both certain general considerations [18], and experimental data, for example, from x-ray spectra, according to which ~ 1 electron is located only in the 4p-states of nickel [19].

observed initial growth and the further reduction in absolute amount of thermal emf are qualitatively explained.

In a similar manner, but by the transition of the Fermi level during its drop to the section of the curve $N(\varepsilon)$ with constant slope, can one explain the linear rise in negative thermal emf after 400° even for Ni_2B. Since for NiB the Fermi level lies beyond the limits of the d-zone, the interzonal transitions for it do not occur and the second term in the parentheses of the expression for α drops out. In this case, a simple temperature-proportional rise in α must occur. This is approximately observed, especially in the region of low temperatures, while the positive sign α is apparently explained by the clear dominance of vacancies in the formation of thermal emf of this boride.

9. Thermal conductivity λ (see table 1, fig. 2) is reduced in a number of Ni_2B, Ni_3B and NiB compounds, while electrical resistance rises. This correlation of these quantities is preserved in the entire studied temperature interval. For Ni_2B and Ni_3B with a rise in temperature, λ drops, while the relationship $\rho(T)$ is close to the straight proportionality. For NiB, on the contrary, λ increases, while the rate of increase in ρ is noticeably reduced. These observations show that for the examined borides, the Wiedemann-Franz law is fulfilled at least qualitatively. This once again indicates the metal nature of their conductance and the dominant role of the electrons in the process of heat transfer.

The rise in heat conductivity of NiB is probably dictated by the gradual reduction in the rate of growth in the electrical resistance as the temperature rises (see fig. 2). As noted in publication [8], none of the known mechanisms for scattering of the current carriers explains this nature of the relationship $\lambda(T)$ and $\rho(T)$. An escape from the difficulty can be found if we assume that in such anomalous, but fairly common cases even for pure transitional metals, with an increase in temperature the number of current carriers increases [8,21]. This increase can occur, for example, through release of a certain number of electrons from participation in the valent bonds. This phenomenon is apparently also associated with a halting in the rise in thermal emf for NiB in the region of high temperatures.

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