Influence of replacement of gadolinium with zirconium on the magnetic properties and hyperfine interactions in $Gd_{1-x}Zr_xCo_2$ compounds

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The magnetic properties and hyperfine fields were determined for the $Gd_{1-x}Zr_xCo_2$ system. It was found that a change in the *d*-electron density due to replacement of gadolinium with zirconium had a strong influence on the magnetic properties and hyperfine interactions. The results of this investigation were described satisfactorily by the hybrid *d*-band approximation.

The search for new magnetic materials has recently been extended to intermetallic compounds formed between rare metals and 3*d* transition metals. In this class of compounds those of particular interest are the Laves phases with the formula RCo_2, in which the magnetic moment of cobalt is induced by the rare-earth sublattice.[1,2] There is as yet no clear physical understanding of the magnetic ordering mechanisms, which are influenced decisively by the occupancy of the *d*-electron hybrid band formed by the 3*d* electrons of cobalt and the 5*d* electrons of the rare-earth.

Important information on the magnetism of these compounds can be provided by simultaneous studies of their magnetic properties and hyperfine interactions, since the distribution of the electron spin density is the dominant factor governing the exchange fields as well as the hyperfine fields at the nuclei.

We shall report an investigation of the magnetic properties and of nuclear magnetic resonance (NMR) at the nuclei of cobalt in $Gd_{1-x}Zr_xCo_2$ compounds. This particular system of compounds (alloys) was selected because the replacement of trivalent gadolinium ions whose outer electron shell is $4f^75s^25p^65d\,6s^2$ with quadrivalent zirconium with the outer electron configuration $4d^25s^2$ alters the *d*-electron density. This should be reflected in the occupancy of the hybrid *d* electron band and have a significant influence on the exchange and hyperfine interactions whose strengths depend on the band-electron polarization.

Our $Gd_{1-x}Zr_xCo_2$ compounds were prepared at the Baikov Institute of Metallurgy of the USSR Academy of Sciences. All the samples were synthesized by the method of arc melting on a copper water-cooled base in an atmosphere of spectroscopically pure helium. Metallographic and x-ray diffraction analyses were carried out. The composition of the compounds was determined by the x-ray fluorescence method. All the $Gd_{1-x}Zr_xCo_2$ compounds were single-phase and had the *C* 15 structure of the $MgCu_2$ type (cubic Laves phases). The magnetization was measured with a pendulum magnetometer between 77 and 800 K in magnetic fields up to 13 kOe and a vibrating-sample magnetometer with a superconducting solenoid in a field up to 45 kOe at temperatures from 4.2 to 300 K. The NMR of ^{59}Co was investigated by the spin echo method.

Figure 1 shows the isotherms of the specific magnetization σ measured at 4.2 K for the $Gd_{1-x}Zr_xCo_2$ compounds. In the case of the compounds with $x = 0.1$–0.8, the $\sigma(H)$ curves exhibited magnetic saturation. An increase in the Zr concentration reduced the magnetization. The compositions with $x = 0.9$ and 0.93 exhibited a linear rise of the magnetization in fields in excess of 20 kOe. In the case of $ZrCo_2$ the $\sigma(H)$ curves were linear throughout the investigated range of fields and temperatures.

Extrapolation to $H \to \infty$ of the magnetization curves plotted as a function of $1/H$ yielded the saturation magnetization. Its values σ_0 determined at 4.2 K decreased linearly on increase in the Zr concentration and vanished at $x = 0.96$ (curve 6 in Fig. 2). The critical concentration for the appearance of ferrimagnetism in these compounds was 4 at.% Gd.

At all the zirconium concentrations the magnetization of the cobalt sublattice was less than that of the gadolinium sublattice so that there was no magnetic compensation temperature in the $\sigma_0(x)$ dependence. The Curie temperature T_C, determined by a thermodynamic method[3] (curve 4 in Fig. 2), varied nonlinearly with the concentration of Zr in $Gd_{1-x}Zr_xCo_2$ and it was found that in the range $x > 0.4$ it fell faster, whereas in the range $x < 0.4$ it fell more slowly on reduction in the Gd content compared with the isostructural $Gd_{1-x}Y_xCo_2$ system[4] (curve 3 in Fig. 2).

The magnetic moment μ_{Co} per cobalt ion at 4.2 K was estimated from the saturation value of the magnetic moment μ_0 calculated per formula unit at 4.2 K. Assuming that the

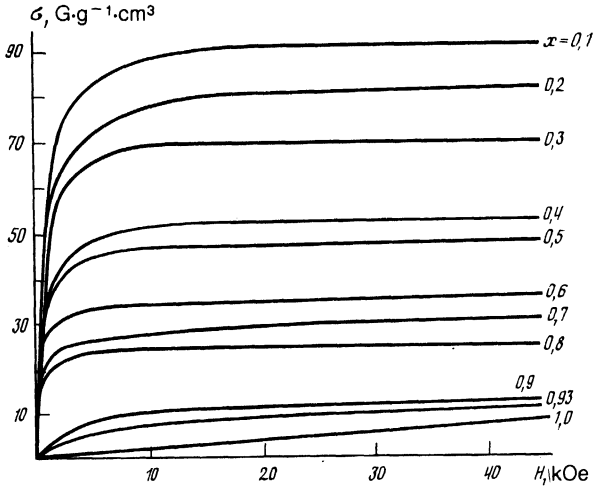

FIG. 1. Isotherms of the specific magnetization obtained at 4.2 K for $Gd_{1-x}Zr_xCo_2$ samples of different compositions.

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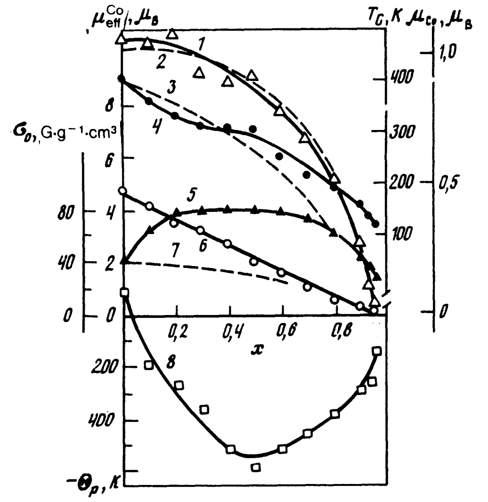

FIG. 2. Magnetic properties of the $Gd_{1-x}Zr_xCo_2$ systems: 1) dependence of the magnetic moment of cobalt on the zirconium concentration in $Gd_{1-x}Zr_xCo_2$; 2) dependence of the magnetic moment of cobalt on the yttrium concentration in $Gd_{1-x}Y_xCo_2$ (Ref. 4); 3) dependence of the Curie temperature on the yttrium concentration in $Gd_{1-x}Y_xCo_2$ (Ref. 4); 4) dependence of the Curie temperature on the zirconium concentration in $Gd_{1-x}Zr_xCo_2$; 5) dependence of $\mu_{\rm eff}^{\rm Co}$ on the zirconium concentration in $Gd_{1-x}Zr_xCo_2$; 6) dependence of the saturation magnetization at 4.2 K on the zirconium concentration in $Gd_{1-x}Zr_xCo_2$; 7) dependence of $\mu_{\rm eff}^{\rm Co}$ on the ytrrium concentration in $Gd_{1-x}Y_xCo_2$; 8) dependence of the paramagnetic Curie temperature on the zirconium concentration in $Gd_{1-x}Zr_xCo_2$.

magnetic moment of Gd was equal to its value for an isolated trivalent ion $\mu_{\rm Gd} = 7\mu_B$ (μ_B is the Bohr magneton), we found from the ferrimagnetic model that

$$\mu_{\rm Co}={}^1/_2[(1-x)\mu_{\rm Gd}-\mu_0]. \qquad (1)$$

The results (curve 1 in Fig. 2) indicated that the value of $\mu_{\rm Co}$ of the compounds with $x > 0.2$ fell in accordance with the parabolic law

$$\mu_{\rm Co}(x)=\mu_{\rm Co}(0)\,[(0{,}96)^2-x^2], \qquad (2)$$

where $\mu_{\rm Co}(0)$ is the value of $\mu_{\rm Co}$ corresponding to $x = 0$. The magnetic moment of cobalt was $\mu_{\rm Co} = 0$ for the compound with $x = 0.96$. Consequently, the magnetic moment of cobalt varied within fairly wide limits from $1.06\mu_B$ ($GdCo_2$) to $0.03\mu_B$ ($Gd_{0.05}Zr_{0.95}Co_2$). The compound $ZrCo_2$ was a Pauli paramagnet. The reduction in $\mu_{\rm Co}$ on increase in the Zr concentration was due to filling of the hybridized *d* band and a reduction in the exchange splitting of the subbands characterized by positive and negative values of the spin.

The integrals representing the intrasublattice and intersublattice exchange interactions in the $Gd_{1-x}Zr_xCo_2$ system were obtained from the measured values of the paramagnetic susceptibility at temperatures above the Curie point right up to 800 K, obtained in a field of 13 kOe. We plotted in Fig. 3 the temperature dependence of the paramagnetic susceptibility of the $Gd_{1-x}Zr_xCo_2$ compounds. In the range $T > T_C$ the reciprocal of the susceptibility of these compounds obeyed the Néel law:[5]

$$\frac{1}{\chi-\chi_p}=\frac{1}{\chi_0}+\frac{T}{C}-\frac{\delta}{T-T_c}, \qquad (3)$$

where χ_p is the Pauli paramagnetic susceptibility and C is the Curie constant. The parameters χ_0, T_C, and δ were found experimentally and depended on the coefficients of the molecular structure. According to the data of Ref. 6, the Pauli paramagnetic susceptibility χ_p of the compounds RCO_2 is negligible compared with the total susceptibility of a sample χ.

The existence of a linear region of the dependences $\chi^{-1}(T)$ made it possible to find experimentally the Curie constant C from the slope of $\chi^{-1}(T)$. The constant C found in this way yielded the effective magnetic moment $\mu_{\rm eff}$ when use was made of the expression relating C and $\mu_{\rm eff}$:

$$C=N_0\mu_{\rm eff}^2/3k_B, \qquad (4)$$

where N_0 is the Avogadro number and k_B is the Boltzmann constant. Knowing the value of $\mu_{\rm eff}$, we could find the effective magnetic moment of cobalt $\mu_{\rm eff}^{\rm Co}$ from the relationship between the magnetic moment of the compound $\mu_{\rm eff}$ and the magnetic moments of the ions in the Gd and Co sublattices:

$$\mu_{\rm eff}^2 = (1-x)^2(\mu_{\rm eff}^{\rm Gd})^2 + 2(\mu_{\rm eff}^{\rm Co})^2. \qquad (5)$$

The values of $\mu_{\rm eff}^{\rm Co}$ obtained in this way are plotted in Fig. 2 (curve 5). We can see that replacement of gadolinium with zirconium first increased $\mu_{\rm eff}^{\rm Co}$ to the maximum value $4.2\mu_B$ for $Gd_{0.5}Zr_{0.5}Co_2$ and this was followed by a fall of $\mu_{\rm eff}^{\rm Co}$ as the zirconium concentration increased. The value $\mu_{\rm eff}^{\rm Co} \approx 2.1\mu_B$ obtained by us for $GdCo_2$ was in good agreement with the results reported in Refs. 5 and 7. It was interesting to note that $\mu_{\rm eff}^{\rm Co}$ for the isostructural system of compounds $Gd_{1-x}Y_xCo_2$ fell monotonically on increase in the yttrium concentration (curve 7 in Fig. 2). The difference

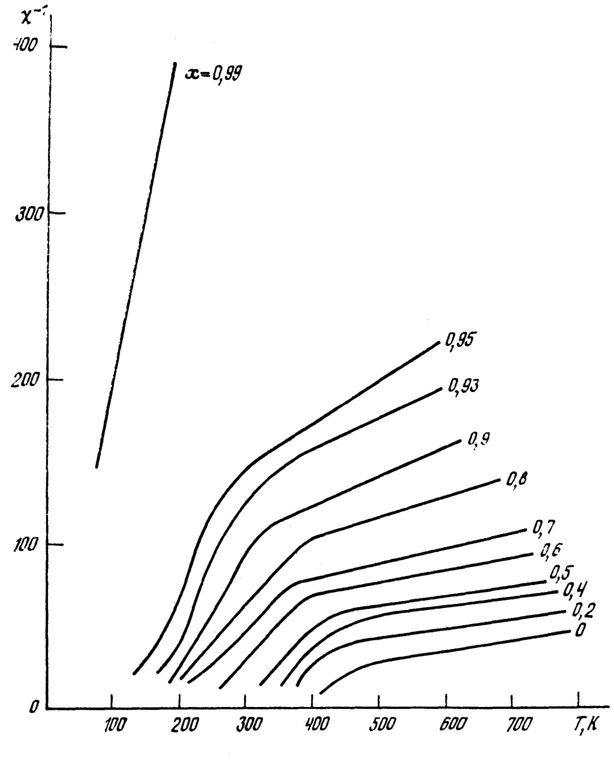

FIG. 3. Temperature dependences of the reciprocal of the paramagnetic susceptibility of samples belonging to the $Gd_{1-x}Zr_xCo_2$ system.

between our system and that containing yttrium was clearly due to the fact that the yttrium atom had the outer electron shell $4d\,5s^2$, whereas the outer shell of zirconium was $4d^2 5s^2$. Consequently, the additional $4d$ electron of the zirconium atom affected strongly the value of $\mu_{\rm eff}^{\rm Co}$.

The Curie temperature T_C also had singularities in the dependence on the composition of $Gd_{1-x}Zr_xCo_2$, compared with the corresponding dependence in the case of $Gd_{1-x}Y_xCo_2$ (curves 3 and 4 in Fig. 2). We determined also the paramagnetic Curie temperature Θ_p at temperatures exceeding considerably T_C (curve 8 in Fig. 2) in the region where the following relationship was obeyed:

$$1/\chi=(T-\Theta_p)/C. \qquad (6)$$

Clearly, Θ_p was a positive quantity for $GdCo_2$, but an increase in the Zr concentration in $Gd_{1-x}Zr_xCo_2$ made it negative and its maximum absolute value was $\Theta_p \approx -570$ K corresponding to $x \approx 0.5$; in the range $x > 0.7$ the absolute value fell.

The measured paramagnetic susceptibility was used to determine the integrals of the intersublattice exchange interactions by a method proposed by Pauthenet[8] and Aleonard.[9] This method was based on a comparison of the experimental $\chi^{-1}(T)$ curve obtained in the range $T > T_C$ with the theoretical dependence described by Eq. (3). We used the experimentally determined coefficients π_0^{-1}, δ, and T_C to find the integrals of the exchange interactions within the gadolinium sublattice ($J_{\rm Gd\text{-}Gd}$), within the cobalt sublattice ($J_{\rm Co\text{-}Co}$), and between the sublattices ($J_{\rm Gd\text{-}Co}$). It was found that

$$J_{\rm Gd-Gd}>0, \quad J_{\rm Co-Co}>0, \quad J_{\rm Gd-Co}<0.$$

In the composition range $0 \leqslant x \leqslant 0.7$ these integrals did not change significantly and a strong rise of their absolute values was observed only in the range $x > 0.7$. For $x = 0.5$, the integrals were

$$J_{\rm Gd-Gd}=3{,}71\ \rm K, \quad J_{\rm Co-Co}=0{,}41\ \rm K, \quad J_{\rm Gd-Co}=-1{,}42\ \rm K.$$

The molecular field coefficients representing the Ge–Co, Co–Co, and Gd–Gd interactions had the following values for $x = 0.5$:

$$n=20{,}1, \quad \alpha=3{,}0, \quad \beta=0{,}24.$$

They also changed little in the composition range $0 \leqslant x \leqslant 0.7$. However, they varied rapidly for compositions with $x > 0.7$. At $x = 0.95$ we found that

$$n=69, \quad \alpha=2{,}53, \quad \beta=0{,}37.$$

As pointed out above, there were also considerable falls of $\mu_{\rm eff}^{\rm Co}$ and Θ_p in the range $x > 0.7$. We could assume that at concentrations $x > 0.7$ the subband $3d\downarrow$ filled rapidly, which reduced the magnetic moment of cobalt and the paramagnetic Curie temperature, but increased the absolute values of the exchange integrals.

A more detailed investigation of the behavior of the local magnetic moment of cobalt and possible changes in the density of states in the d-electron band was made by determination of the NMR frequency and of the longitudinal nuclear relaxation time of the ^{59}Co nuclei. It is clear from Fig. 4 that replacement of gadolinium with zirconium reduced the NMR frequency and the nature of the composition dependence of this frequency was the same as that of the composition dependence of the Curie temperature (curve 4 in Fig. 2). In the case of samples with $x > 0.2$ the lf wing of the main signal acquired an additional satellite, which was due to the formation of a nonmagnetic state of cobalt.[10] The resonance field of the "magnetic" state of cobalt could be represented by a sum of two oppositely directed contributions, the first of which was due to the exchange polarization of the closed s shells of the Co atom with an intrinsic magnetic moment and the second was due to the polarization of the conduction electrons. The magnitude of the second contribution could be found by assuming that the resonance field of the "nonmagnetic" peak was entirely due to the conduction electrons. Interpolation of the average hyperfine field to the value $x = 1$ ($ZrCo_2$) gave $H_{\rm int} = 48$ kOe. The contribution of the gadolinium sublattice was found from the difference between the values of $H(x)$ for $x = 0$ and $x = 1$ and it amounted to 13 kOe, which was half the value for $GdAl_2$ (Ref. 11). The appearance of the nonmagnetic state of cobalt was a consequence of the transfer of the d valence electrons of zirconium to the cobalt atoms.

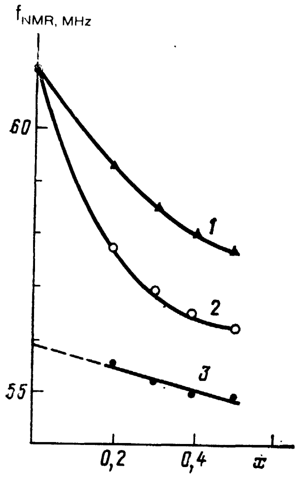

FIG. 4. Dependence of the NMR frequency of ^{59}Co at 77 K and the zirconium concentration: 1) first satellite; 2) center of gravity; 3) second satellite of the resonance profile.

A similar transfer in the magnetic state altered the density of states $N(E)$ in the hybrid d band. This was supported directly by the measured longitudinal nuclear relaxation time T_1 of the magnetic satellite (Fig. 5). It is clear from Fig. 5 that replacement of gadolinium with zirconium reduced

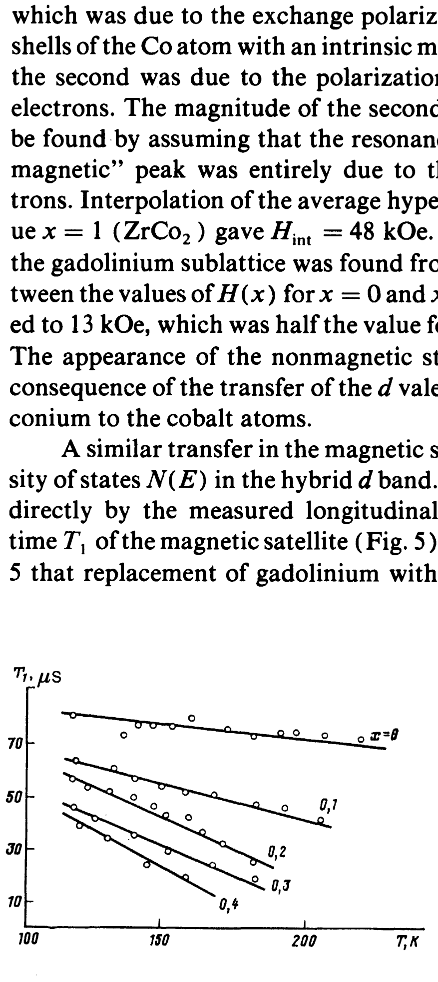

FIG. 5. Temperature dependences of the longitudinal nuclear relaxation time of ^{59}Co in samples of the $Gd_{1-x}Zr_xCo_2$ system.

the relaxation time T_1. It was known from Ref. 12 that this relaxation time obeyed $T_1 \propto [H_{\rm hf}(d) N_d(E_F)]^2$, where $H_{\rm hf}(d)$ is the hyperfine field due to the d-electron polarization, whereas $N_d(E_F)$ is proportional to the density of states at the Fermi level in the d band.

Therefore, on the one hand the magnetic moment of cobalt found from our magnetic measurements and from the composition dependence of the NMR of ^{59}Co varied little in the range $0<x<0.5$ (curve 1 in Fig. 2), whereas on the other hand, the nuclear relaxation time indicated that the density of states in the d band changed quite significantly. This was possible only when the hybrid d band was formed. In the case of the $3d$ band there were no changes in the state of cobalt and the additional d valence electrons of zirconium filled the $4d$ band of zirconium which was a component of the new hybrid band.

An indirect confirmation of the modification of the hybrid d-electron band of the compounds $Gd_{1-x}Zr_xCo_2$ was provided by a modified model of Wohlfarth,[13] according to which the Curie temperature of the compounds with low gadolinium concentrations should obey

$$T_C = T_F[\Gamma N(E_F) - 1]^\tau,$$

where

$$T_F = \frac{1}{6}\pi^2 k_B^2 \left\{ \left[\frac{N'(E_F)}{N(E_F)} \right]^2 - \frac{N''(E_F)}{N(E_F)} \right\},$$

where Γ is the exchange energy per unit volume and N is the density of states at the Fermi level. According to the modification of the Wohlfarth model, the parameter τ varies from $\tau = 1/2$ to $\tau = 1$.[14] One of the consequences of a thermomagnetic analysis of the magnetic ordering is the dependence of the saturation magnetization on T_C; in the case when $\tau = 1$, we have $\sigma_0^2 \propto T_C$.

Figure 6 gives the dependence $\sigma_0^2(T_C)$. It is clear from this figure that the $Gd_{1-x}Zr_xCo_2$ system exhibits two ranges of compositions ($x<0.5$ and $x>0.5$) in which the coefficient of proportionality between σ_0^2 and the quantity $T_F[N(E_F)\Gamma - 1]^2$ remains constant, but changes abruptly on transition from one region to the other. This result is in agreement with the above data indicating major changes in the exchange integrals when the zirconium concentration is in the range $x > 0.7$.

It follows from an analysis of the composition dependence of the magnetic ordering (Curie) temperature T_C (Ref. 15), carried out by the molecular field method, that the terminal ($x = 0$) compound of the $Gd_{1-x}Zr_xCo_2$ system has a Curie temperature T_C which can be found from the equation

$$\left(\beta^* - \frac{k_B T_C}{2\mu_{Co}^2}\right)\left(\alpha^* - \frac{7k_B T_C}{3\mu_{Gd}^2}\right) - \gamma^{*2} = 0,$$

where α^*, β^*, and γ^* are constants describing the interactions of the Gd–Gd, Co–Co, and Gd–Co pairs. The magnitudes of the contributions of the "partial" exchange interactions to the overall temperature are governed by the constants α^*, β^*, and γ^* multiplied by the appropriate partial derivatives with respect to T_C. It was found in Ref. 15 that

FIG. 6. Behavior of the function $\sigma_0^2(T_C)$ for the $Gd_{1-x}Zr_xCo_2$ system.

$$\alpha^* \frac{\partial T_C}{\partial \alpha^*} \approx 60\,\text{K}, \quad \beta^* \frac{\partial T_C}{\partial \beta^*} = 143\,\text{K}, \quad \gamma^* \frac{\partial T_C}{\partial \gamma^*} = 199\,\text{K},$$

i.e., the intersublattice interaction predominates in the determination of the numerical value of T_C.

According to the molecular field theory, when we go over to quasibinary compounds, i.e., when gadolinium atoms are replaced with nonmagnetic yttrium or zirconium atoms, the Curie temperature $T_c(x)$ is governed by the effective values $\alpha_{\rm eff} = \alpha^*(1-x)$ and $\gamma_{\rm eff} = \gamma^*(1-x)$, which implies a linear reduction in the Curie temperature as a result of dilution of the gadolinium sublattice. The experimentally observed (curve 4 in Fig. 2) non linear dependence $T_c(x)$ shows that the values of the exchange parameters α^* and γ^* vary with the concentration of the nonmagnetic component and the molecular field approximation is then insufficient.

Since the values of T_C for the quasibinary compounds $Gd_{1-x}Zr_xCo_2$ are governed primarily by the intersublattice interaction and by the $3d$–$3d$ exchange, it is more correct to describe the magnetic ordering in the approximation known as the combined model,[16] according to which T_C is described by the following expression:

$$T_C = \frac{S(S+1)}{3k_B N_0 g^2} J_{\rm eff}^2 \frac{N_d(E_F)}{1 - \Gamma N_d(E_F)},$$

where S is the value of the spin moment of gadolinium and g is the Landé factor.

The physical meaning of the combined model is that the atomic magnetic moments of the rare-earth sublattice are regarded as localized and the $3d$ sublattice is described by the exchange-enhanced suscepbility

$$\chi(E) = \frac{\chi_{\rm par}}{1 - \Gamma N}$$

where $\chi_{\rm par}$ is the paramagnetic susceptibility of the impurity. The total atomic energy can then be represented in the form $2J_{\text{eff}} sS$, where s is the spin of the oscillating d electrons responsible for the intersublattice interaction.[17]

The nonlinear nature of the dependence $T_C(x)$ is then governed by the expression $1 - \Gamma N(E_F)$. Since $\Gamma N(E_F)$ for the RCO_2 compound is close to unity,[18] small changes in the density of states and a reduction in the magnetic interaction energy are sufficient to account for the observed composition dependence of T_C in the compounds investigated by us.

Our analysis of the magnetic properties and hyperfine interactions in the $\mathrm{Gd}_{1-x}\mathrm{Zr}_x\mathrm{Co}_2$ system thus demonstrated that the investigated compounds (alloys) can be described quite satisfactorily assuming the band nature of the d sublattice. An indirect confirmation was obtained of the existence of a hybrid d-electron band and of the transfer of the d electrons from zirconium to cobalt atoms. One should point out that the use of the combined model leaves unsolved the problem of the physical nature of the effective exchange integral of the f–d interaction. It was found that a change in the d-electron density in the $\mathrm{Gd}_{1-x}\mathrm{Zr}_x\mathrm{Co}_2$ system affected the magnetic properties of these compounds.

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