

Curie Temperatures of Substituted Rare Earth–Aluminium $L_{1-x}R_xAl_2$ Compounds

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The experimental Curie temperatures of the substituted rare earth–aluminium $L_{1-x}R_xAl_2$ compounds (with rare earths L, R: La, Gd, Tb, Dy, Ho, Er, Tm, Lu, and Y) scale linearly with the de Gennes factor. The magnetic rare-earth sublattice is treated as being composed of two magnetic subsystems: the $4f$ subsystem of L^{3+} or R^{3+} ions and the $5d$ subsystem of band electrons. The de Gennes factor $G = (g - 1)^2 J(J + 1)$, with g as the Landé factor and J as the total angular momentum quantum number, reflects the $4f$ shell quantum properties of the L^{3+} or R^{3+} ion. A formula introducing the linear dependence of the Curie temperature on the de Gennes factor for the substituted rare earth–aluminium compounds is derived with consideration of the Zener-type $4f$ – $5d$ exchange interaction within the frame of the molecular field model. The obtained formula was tested for a number of different members of the heavy rare earth–aluminium intermetallic series. A relative constancy of the $4f$ – $5d$ exchange interaction across the considered $L_{1-x}R_xAl_2$ series has been deduced. The formula can easily be adapted also to describe the non-linear dependences of the Curie temperatures on the de Gennes factor.

topics: substituted intermetallics, rare earth–aluminium, Curie temperature formula, linear dependence

1. Introduction

Rare earth(R)– $3d$ transition metal(M) compounds, with R = La, Gd, Tb, Dy, Ho, Er, Tm, Lu, and Y, are typically treated as two-sublattice metallic ferrimagnets [1, 2]. A variety of their useful properties continuously gains scientific and practical interest in the studies of these materials. Atoms of the lanthanide series with the electronic configuration Xe $4f^n 5d^1 6s^2$ (or yttrium with the configuration Kr $4d^1 5s^2$) in intermetallics transfer their $5d^1 6s^2$ (or $4d^1 5s^2$) electrons to the electronic bands. As the $5d^1 6s^2$ (or $4d^1 5s^2$) band electrons do not fulfil the Stoner criterion autonomously, the lanthanum or yttrium metals are not magnetically ordered substances [3, 4]. However, in the R–M intermetallics, these band electrons are polarized by the $4f$ -magnetic moments or the $3d$ -magnetic moments and as a result their induced band magnetic moments can even form a Slater–Pauling-type dependence [5, 6].

The RM₂-type intermetallics considered below stabilize in a face-centered cubic Laves $Fd\bar{3}m$, C15, MgCu₂-type structure described in detail elsewhere [1, 7]. In this structure, the 8a sites are occupied by the rare-earth atoms (R — crystal sublattice) and the 16d sites are occupied by the $3d$ -transition metal atoms (M — crystal sublattice).

An important part of the R–M studies is related to the magnetic ordering temperatures of these materials. To explain magnetism in the R–M compounds, mechanisms of the long range Ruderman–Kittel–Kasuya–Yosida (RKKY) exchange interactions or of the local-type exchange interactions have been discussed in detail elsewhere [1, 2, 8].

In the R–M intermetallics, the Curie temperatures are well described by the empirical Taylor formula $T_C = T_{C-3d} + T_{C-4f}$, where the T_{C-3d} component originates from the M sublattice and the $T_{C-4f} = BG$, the linear element against the de Gennes factor G with B constant, originates from the R sublattice with this one sort of rare-earth atoms [1]. This formula has been derived using the Zener-type model of exchange interactions applied to the R–M ferrimagnets [9, 10]. The de Gennes factor $G = (g - 1)^2 J(J + 1)$, with the g — the Landé factor and J as the total angular momentum quantum number, reflects the $4f$ -shell quantum properties of the R^{3+} ion [1, 2].

Currently, there is a sound experimental test which shows that the magnetic ordering temperatures T_C of the substituted $L_{1-x}R_xAl_2$ compounds with L, R rare-earth components scale linearly with the G -factor [11–21]. In these compounds, the L/R rare-earth atoms occupy the 8a sites and the non-magnetic Al atoms occupy the 16d crystal positions.

No suitable T_C -formula exists for this type of compound to date. Thus the attempt of this paper is to derive a formula for the magnetic ordering temperature of the substituted $L_{1-x}R_xAl_2$ intermetallics (L, R: La, Gd, Tb, Dy, Ho, Er, Tm, Lu, and Y) treated T_C as a function of the formally introduced G_L and G_R de Gennes factors. Also in this case, the Zener-type model of the exchange interactions has been adapted for this purpose and the obtained formula has been tested within the various experimental T_C data.

2. Ordering temperature formula

Following the Zener-type approach, an exchange interaction between the spin \mathbf{S} of the localized $4f$ -shell and the band electron polarization \mathbf{s} can be expressed as [9, 10, 22, 23]:

$$\mathcal{H} = -2K_{4f-ce}\mathbf{S} \cdot \mathbf{s}. \quad (1)$$

The spins and electron polarizations or their thermal average values can be treated as vectors in the calculations. During further calculations, the projection formula $\mathbf{S} = (g - 1)\mathbf{J}$, where g is the Landé factor and \mathbf{J} is the angular momentum of the $4f$ -shell of the L^{3+} or R^{3+} ion, is applied. Moreover, the magnetic moment of the $4f$ -shell (in μ_B — the Bohr magnetons) equals $m = gJ$ [1, 24, 25]. The K_{4f-ce} is the exchange integral parameter, which for the heavy rare earths couples \mathbf{S} and \mathbf{s} ferromagnetically [1, 2, 24].

The rare-earth atoms transfer their $5d^16s^2$ electrons to the band, therefore at the 8a crystal sites the L^{3+} , R^{3+} ions reside. The localized electrons of the $4f$ -shell of these ions are well shielded by the more outer $5sp$ atomic-like electrons from the rest of the crystal lattice [26, 27]. Thus, the direct $4f-4f$ exchange interactions between the neighboring rare-earth ions are practically absent. As the $5d6s$ electrons partially reside within rare-earth ions, magnetic polarization of these electrons by a direct $4f-5d(6s)$ exchange interaction occurs and therefore these electrons transfer exchange interactions to L^{3+} , R^{3+} neighbors in the crystal lattice [1]. The $4f$ -shells form local magnetically polarizing centers for the band $5d6s$ electrons, whereas these band electrons form a medium to acquire the magnetic polarization throughout the entire rare-earth sublattice.

Actually, it is known that the magnetic moment of the polarized s -conduction electrons is small (less than $0.025 \mu_B$), and consequently these electrons can be ignored in further calculations [28]. Therefore, only the band-type $5d$ -electrons with the K_{4f-5d} exchange interaction parameter are taken into account in the calculations. The magnetic moment m_{5d} is considerable but most often $m_{5d} \ll m$, as discussed elsewhere [29].

In the Zener-type model of the exchange interactions, the number of crystal nearest neighbors is not explicitly important. In this case, there is one $5d^1$

electron acting as the effective nearest neighbor of the L^{3+} or R^{3+} ion. Moreover, one L^{3+} or R^{3+} ion acting as the nearest neighbor per one $5d^1$ band electron occurs. This pair locally creates a magnetic bonding with energy $E_{4f-5d} = E_{5d-4f} = K_{4f-5d}Ss = K_{5d-4f}sS$.

The $5d$ -band matter which straggles the 8a crystal places of the sublattice additively collects the local magnetic polarizations or more generally accumulates the local magnetic bonds. Consequently, the magnetism of the rare-earth sublattice is mediated via this $5d$ -band medium. Especially, the $5d$ -band summarizes these bonds to establish the common Curie temperature for the whole crystal lattice. This property supports the method of deriving the formula for the magnetic ordering temperature of the substituted compounds.

Following (1), the Hamiltonian of the $L_{1-x}R_xAl_2$ system can be presented as an additive formula composed of two parts

$$\mathcal{H} = -\frac{2K_{L;4f-5d}}{N} \sum_{i=1}^{i=N_{L;4f}} \mathbf{S}_{L;4f} \mathbf{s}_{L;5d} - \frac{2K_{R;4f-5d}}{N} \sum_{j=1}^{j=N_{R;4f}} \mathbf{S}_{R;4f} \mathbf{s}_{R;5d}, \quad (2)$$

where the letter L before the semicolon denotes the L component, the letter R denotes the R component, while the N normalization number is the number of all 8a crystal sites. Moreover, $N_{L;4f} = (1-x)N$, $N_{R;4f} = xN$ is the number of the L atoms and of the R atoms populating the rare-earth sublattice, respectively. The $K_{L;4f-5d}$, $K_{R;4f-5d}$ parameters denote the $4f-5d$ exchange interaction integrals characteristic for the L, R component, correspondingly.

Concerning the Hamiltonian (2), the energy of magnetic ordering E can be written in the form

$$E = E_L + E_R, \quad (3)$$

where E_L represents the L contribution and E_R represents the R contribution. At the magnetic phase transition, the magnetic ordering energy equals the thermal energy: $E = k_B T_C$ (k_B — the Boltzmann constant) and (3) can be rewritten as

$$T_C = T_{CL} + T_{CR}, \quad (4)$$

where T_C , T_{CL} and T_{CR} are the temperatures corresponding to the energies.

At first glance, the $L_{1-x}R_xAl_2$ system, in which only one crystal sublattice is occupied by magnetic atoms, seems to be similar to a ferromagnet. However, to treat these intermetallics as a ferromagnet is not the way to approach the formula with a proportionality between T_C and G . At this stage, supporting it is the fact the $4f$ -rare-earth ions and the $5d$ -band electrons form, to a high level, two distinct magnetic subsystems with the ferromagnetic $K_{4f-5d} = K_{5d-4f}$ coupling for each (L or R) component, in the shape of the two-sublattice ferrimagnet.

The simplest way is to treat the calculation of the L, R components in (2) separately. Therefore, the molecular fields for the 4*f*, 5*d* magnetic subsystems, considered in analogy to the two magnetic sublattices of the ferrimagnet, appendant to the L component, following the method presented previously, can be written as follows [9, 10, 30]:

$$H_{L;4f} = H - 0 - b_{L;4f-5d}M_{L;5d} \quad (5)$$

$$H_{L;5d} = H - b_{L;5d-4f}M_{L;4f} - b_{L;5d-5d}M_{L;5d}, \quad (6)$$

where $H_{L;4f}$ is the molecular field acting on the well localized 4*f* magnetic moments of the L component, $H_{L;5d}$ is the molecular field acting on the band 5*d*-electrons of the L component, H is the strength of the applied external magnetic field. Moreover, $b_{L;i,j}$ are the appropriate molecular field coefficients, $M_{L;4f}$ is the 4*f*-magnetic moment which belongs to the L component and $M_{L;5d}$ is the 5*d*-magnetic moment which belongs to the L component. Since the direct 4*f*-4*f* exchange interaction between L-L nearest neighbors can be excluded, thus the element $b_{L;4f-4f}M_{L;4f}$ in (5) is approximated to zero [26, 27]. Therefore, after this reduction, the above equations correspond to the pure Zener model to be applied [22, 23]. A similar system of (5) and (6) can also be introduced for the R component of the rare-earth sublattice.

Summarizing, in the above set of (5) and (6), $b_{L;4f-5d}$ is the molecular field coefficient corresponding to the molecular field acting on the (L; 4*f*)-magnetic moment from the side of the 5*d*-band electrons and reciprocally $b_{L;5d-4f}$ is the

coefficient which corresponds to the molecular field acting on the 5*d*-band electron originated by the (L; 4*f*) localized magnetic moment. The molecular field coefficients $b_{L;4f-5d}$ and $b_{L;5d-4f}$ can be expressed as [9, 10, 30]:

$$b_{L;4f-5d} = \frac{(g_L - 1)}{g_L \mu_B^2} \frac{2K_{L;4f-5d} u_{4f-5d}}{g_{5d} N_{L;5d}} \quad (7)$$

and

$$b_{L;5d-4f} = \frac{(g_L - 1)}{g_L \mu_B^2} \frac{2K_{L;5d-4f} u_{5d-4f}}{g_{5d} N_{L;4f}}, \quad (8)$$

where g_{5d} , g_L are the Landé factors of 5*d*-electrons, 4*f*-shells, $N_{L;5d}$, $N_{L;4f}$, as mentioned above, are the numbers of band electrons in the 5*d*-subsystem, and of ions in the 4*f*-subsystem, respectively. Following the discussion above, the numbers of nearest neighbors $u_{4f-5d} = u_{5d-4f} = 1$.

The magnetic moments of the magnetic subsystems above the ordering temperature can be expressed as follows [9, 10, 30]:

$$M_{L;4f} = \frac{C_{L;4f}}{T} H_{L;4f}, \quad (9)$$

$$M_{L;5d} = N_{L;5d} \chi_{L;5d} H_{L;5d}, \quad (10)$$

where $C_{L;4f}$ is the Curie constant of the L³⁺ ions and $\chi_{L;5d}$ is the band susceptibility per 5*d*-electron. The Curie constant can be expressed by [30]:

$$C_{L;4f} = \frac{g_L^2 \mu_B^2}{3k_B} N_{L;4f} J_L (J_L + 1). \quad (11)$$

Above, the set of (9) and (10) proper to the L component considering (5) and (6) can be rewritten in a matrix form $[B_L][M_L] = [C_L]$:

$$\begin{bmatrix} T & C_{L;4f} b_{L;4f-5d} \\ N_{L;5d} \chi_{L;5d} b_{L;5d-4f} & 1 + N_{L;5d} \chi_{L;5d} b_{L;5d-5d} \end{bmatrix} \times \begin{bmatrix} M_{L;4f} \\ M_{L;5d} \end{bmatrix} = \begin{bmatrix} C_{L;4f} H \\ N_{L;5d} \chi_{L;5d} H \end{bmatrix}. \quad (12)$$

The symbol T in (9)–(12) indicates the absolute temperature of the L_{1-x}R_xAl₂ compound.

At the magnetic ordering temperature, the inverse magnetic susceptibility should approach the value of zero which is equivalent to the condition $\text{Det}[B_L] = 0$ [30].

This condition can be used to approach a formula for the Curie temperature contribution $T_{CL;4f}$ of the magnetic L component. After the standard calculation, the $T_{CL;4f}$ -contribution of the L_{1-x}R_xAl₂ system can be expressed as

$$T_{CL;4f} = \frac{N_{L;5d} \chi_{L;5d} C_{L;4f} b_{L;4f-5d} b_{L;5d-4f}}{1 + N_{L;5d} \chi_{L;5d} b_{L;5d-5d}}. \quad (13)$$

In a typical case, the small $b_{L;5d-5d}$ coefficient can be neglected (5*d* electrons do not fulfil the Stoner criterion autonomously) and the formula for the Curie temperature contribution takes the simple form

$$T_{CL;4f} = B_{L;5d} K_{L;4f-5d}^2 G_L, \quad (14)$$

where $B_{L;5d}$ is the constant which equals

$$B_{L;5d} = \frac{4}{3k_B \mu_B^2} \frac{\chi_{L;5d} u_{5d-4f} u_{4f-5d}}{g_{5d}^2} = \frac{4}{3k_B \mu_B^2} \frac{\chi_{L;5d}}{g_{5d}^2} \quad (15)$$

and

$$G_L = (g_L - 1)^2 J_L (J_L + 1) \quad (16)$$

is the de Gennes factor of the L component [25].

Taking into account $\text{Det}[B_R] = 0$, after calculations analogous to (5)–(16), the formula $T_{CR;4f}$ for the R contribution to the Curie temperature like (14) can be obtained.

Assuming that $\chi_{L;5d}$ for the L component is equal to $\chi_{R;5d}$ for the R component, it can be seen that $B_{L;5d} = B_{R;5d} = B_{5d}$; see (15).

Concerning the discussion above, both the L component and the R component throughout the local-type 4*f*-5*d* exchange interactions magnetically polarize their common 5*d*-band, thus introducing the

common long range magnetic order and consequently the common magnetic phase transition at the same Curie temperature. For the studied compounds, this mechanism is scaled by the substitution x -parameter.

Following the additive Hamiltonian (2), and also (3), (4) and considering the above mentioned conditions for determinants, the formula for the Curie temperature T_C of the $L_{1-x}R_xAl_2$ system can be written as the equation

$$T_C = (1-x)T_{CL;4f} + xT_{CR;4f} = \quad (17)$$

$$(1-x)B_{L;5d}K_{L;4f-5d}^2G_L + xB_{R;5d}K_{R;4f-5d}^2G_R.$$

It can be noted that the $(1-x)$, x parameters denote the L, R contributions to the common T_C — the Curie temperature, respectively.

Assuming that $K_{L;4f-5d}^2 = K_{R;4f-5d}^2 = K_{4f-5d}^2$ is constant across the heavy rare-earth series (similarly to results for the exchange interaction parameters for the RAl_2 system presented in [1]), the Curie temperature formula takes the simplified form

$$T_C = B_{5d}K_{4f-5d}^2[(1-x)G_1 + xG_2] =$$

$$B_{5d}K_{4f-5d}^2G = BG. \quad (18)$$

Here, G is the de Gennes factor, averaged across the rare-earth crystal sublattice and the parameter $B = B_{5d}K_{4f-5d}^2$, which contains the squared exchange integral, similarly to the other results presented elsewhere [8, 25, 31].

For the rare-earth non-magnetic constituent L, like La, Lu, Y, the $K_{L;4f-5d}$ parameter equals zero and then the T_C formula reduces to the second element of (18). It can be added that (17) can easily be extended for more than two components present in the rare-earth sublattice.

3. Curie temperatures of (L/R)Al₂

Figure 1 presents the Curie temperature T_C against the averaged de Gennes factor G for the compounds with the L/R substitution in the rare-earth sublattice (C15, 8a sites) and with the non-magnetic aluminium atoms in the transition metal sublattice (C15, 16d sites), namely for: $La_{1-x}Gd_xAl_2$ (triangles) [14, 15], $Y_{1-x}Gd_xAl_2$ (circles) [13, 14], $Lu_{1-x}Gd_xAl_2$ (squares) [14, 15], $Dy_{1-x}Gd_xAl_2$ (rotated squares) [12, 17], $Dy_{1-x}Tb_xAl_2$ (triangles pointing left) [16], $Ho_{1-x}Tb_xAl_2$ (triangles pointing right) [19], $Er_{1-x}Tb_xAl_2$ (hexagons) [20], $Dy_{1-x}Er_xAl_2$ (stars) [21]. Similarly, the figure also contains the Curie temperatures for the RAl_2 compounds. The RAl_2 compounds can be treated as the fully substituted $L_{1-x}R_xAl_2$ intermetallics ($x = 1$) with $R=La, Gd, Tb, Dy, Ho, Er, Tm, Lu$ and Y (inverted triangles) [11, 12, 18].

The Curie temperatures for the portman-teau of intermetallics are well described using the common linear numerical formula: $T_C = [11.48(0.14)G - 12.38(1.25)]$ K. Consequently,

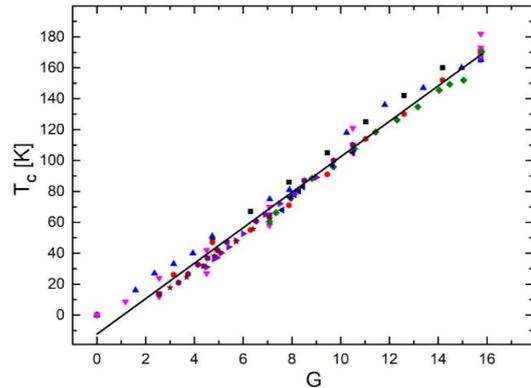


Fig. 1. The experimental Curie temperatures T_C collected for: $La_{1-x}Gd_xAl_2$ (dark blue triangles), $Y_{1-x}Gd_xAl_2$ (red circles), $Lu_{1-x}Gd_xAl_2$ (black squares), $Dy_{1-x}Gd_xAl_2$ (dark green rotated squares), $Dy_{1-x}Tb_xAl_2$ (dark blue triangles pointing left), $Ho_{1-x}Tb_xAl_2$ (violet triangles pointing right), $Er_{1-x}Tb_xAl_2$ (purple hexagons), $Dy_{1-x}Er_xAl_2$ (brown stars) and for RAl_2 (R — rare-earth) compounds (magenta inverted triangles) approximated by the linear T_C -dependence vs the average G -factor. References for the experimental data are presented in the text.

comparing this numerical formula and the expression (18) the parameter $B = 11.48(0.14)$ K is obtained. The numbers in round brackets denote the numerical fitting errors. The small negative intercept parameter (approximately 7% of the maximal T_C -value) in the numerical formula can be ascribed to the distribution of the experimental T_C -points in part and mainly to a little upward deviation of experimental points from linearity in the less represented experimental data in the G -area near to zero. It can be carefully deduced that the T_C vs G linearity does not necessarily appear for the low G -values.

It can be stated that the numerical fitting of the T_C -data for the particular series of compounds introduces a bundle of almost parallel lines closely situated to each other. In fact, a certain insignificant distribution of the B parameters occurs. From the fitted data of the individual series it follows that the resulting B -parameters are located between $B = 10.82(0.33)$ K for the $Y_{1-x}Gd_xAl_2$ series and $B = 12.93(0.15)$ K for the $Ho_{1-x}Tb_xAl_2$ compounds.

It can be added that the sporadic results of measurements with weakly non-linear $T_C(G)$ -dependences are also to be evidenced in literature, as for instance, for the $Dy_{1-x}Y_xAl_2$ and $Tm_xDy_{1-x}Al_2$ series [32, 33].

4. Summary and discussion

In order to derive the Curie temperature formula for the $L_{1-x}R_xAl_2$ compounds, the magnetic rare-earth crystal sublattice was split into two

subsystems: the subsystem of the heavy rare-earth L^{3+} or R^{3+} ions and the subsystem of the $5d$ -band electrons. During calculations, the rare-earth sublattice was treated as a two-sublattice ferrimagnet with the Zener-type model of the exchange interactions between the above mentioned subsystems.

The derived (18) introduces the linear dependence between the Curie temperature and the de Gennes factor. It can be noted that this formula contains the squared exchange integral attended by the magnetic susceptibility in accordance with similar results which are known, for R–M intermetallics or for the RKKY-magnetic systems, as discussed for instance in [8, 25, 31].

The expression was tested for a number of different members of the rare earth–aluminium series. The Curie temperature scales linearly well with the de Gennes factor and practically one slope (B -parameter) of the T_C line appears for the series treated as a whole. From this linearity, it can be expected that the electron band magnetic susceptibility χ_{5d} (see (15)) should be constant for all considered compounds. Consequently, the parameter K_{4f-5d} (see (18)) should also be constant across the series. As pointed out above, a constancy or almost constancy of the exchange integral parameter in the dialuminides derived across the heavy rare-earth series by different measurement methods is presented elsewhere [1]. It seems that this result can support the constancy of the K_{4f-5d} parameter deduced from the T_C line. To discuss this problem in detail, sound future *ab initio* studies would be helpful.

The Curie temperature formula in the extended form (17) is a suitable tool to describe dependences which are more complex than linear dependences. It at least enables considering a nonlinear dependence of the K_{4f-5d} parameter across the heavy rare-earth series or considering differences between the $K_{L;4f-5d}$ and the $K_{R;4f-5d}$ parameters. A task which would be interesting to study further is the deviation from linearity of the Curie temperature dependences. It could be performed both by experimental and band calculation methods. As mentioned above, the up to date experimental evidence of the non-linear dependence of the Curie temperature against the de Gennes factor is poor and only few literature results can be found [32, 33].

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