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

J. Pszczola*

Department of Experimental Physics, Faculty of Mathematics and Applied Physics, Rzeszów University of Technology, al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland

Received: 22.02.2021 & Accepted: 22.04.2021

Doi: 10.12693/APHysPolA.140.72

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 $G = (g - 1)^2J(J + 1)$, 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.

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 $4f^{14}5d^16s^2$ (or yttrium with the configuration Kr $4d^15s^2$) in intermetallics transfer their $5d^16s^2$ (or $4d^55s^2$) electrons to the electronic bands. As the $5d^16s^2$ (or $4d^55s^2$) 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 RM$_2$-type intermetallics considered below stabilize in a face-centered cubic Laves $Fd\bar{3}m$, $C15$, MgCu$_2$-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 $G = (g - 1)^2J(J + 1)$, with $g$ — 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.
2. Ordering temperature formula

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

$$\mathcal{H} = -2K_{4f-ee} S \cdot s.$$  \hspace{1cm} (1)

The spins and electron polarizations or their thermal average values can be treated as vectors in the calculations. During further calculations, the magnetic moment of the $4f$-shell (in $\mu_B$ — the Bohr magnetons) equals $m = gJ$ [1, 24, 25]. The $K_{4f-ee}$ is the exchange integral parameter, which for the heavy rare earths couples $S$ and $s$ 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 $5d$ 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 $5d$ band electron occurs. This pair locally creates a magnetic bonding with energy $E_{4f-5d} = E_{5d-4f} = K_{4f-5d} S s = K_{5d-4f} S S$.

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 $L_1-xR_xAl_2$ system can be presented as an additive formula composed of two parts

$$\mathcal{H} = -\frac{2K_{L4f-5d}}{N} \sum_{i=1}^{N_{L4f}} s_{L4f} s_{L5d} - \frac{2K_{R4f-5d}}{N} \sum_{j=1}^{N_{R4f}} s_{R4f} s_{R5d},$$ \hspace{1cm} (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, $N_{L4f} = (1-x)N$, $N_{R4f} = xN$ is the number of the $L$ atoms and of the $R$ atoms populating the rare-earth sublattice, respectively. The $K_{L4f-5d}$, $K_{R4f-5d}$ 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

$$E = E_L + E_R,$$ \hspace{1cm} (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

$$T_C = T_{CL} + T_{CR},$$ \hspace{1cm} (4)

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

At first glance, the $L_1-xR_xAl_2$ 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 4f, 5d 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]:

\[ H_{L;4f} = H - b_{L;4f} - 5dM_{L;5d} \] (5)
\[ H_{L;5d} = H - b_{L;5d} - 4fM_{L;4f} - b_{L;5d} - 5dM_{L;5d} \] (6)

where \( H_{L;4f} \) is the magnetic field acting on the well localized 4f magnetic moments of the L component, \( H_{L;5d} \) is the molecular field acting on the band 5d-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 4f-magnetic moment which belongs to the L component and \( M_{L;5d} \) is the 5d-magnetic moment which belongs to the L component. Since the direct 4f–4f exchange interaction between L-L nearest neighbors can be excluded, the element \( b_{L;4f} - 4fM_{L;4f} \) 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-4f)-magnetic moment from the side of the 5d-band electrons and reciprocally \( b_{L;5d} - 4f \) is the coefficient which corresponds to the molecular field acting on the 5d-band electron originated by the (L-4f) localized magnetic moment. The molecular field coefficients \( b_{L;4f} - 5d \) and \( b_{L;5d} - 4f \) can be expressed as [9, 10, 30]:

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

and

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

where \( g_{sd} \), \( g_L \) are the Landé factors of 5d-electrons, 4f-shells, \( N_{L;5d}, N_{L;4f} \), as mentioned above, are the numbers of band electrons in the 5d-subsystem, and of ions in the 4f-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]:

\[ M_{L;4f} = \frac{C_{L;4f}}{\chi_{L;4f} H_{L;4f}} \] (9)
\[ M_{L;5d} = N_{L;5d} \chi_{L;5d} H_{L;5d} \] (10)

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

\[ C_{L;4f} = \frac{g_L^2 \mu_B^2}{8} N_{L;4f} J_L (J_L + 1) \] (11)

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

\[ \begin{bmatrix} T \\ N_{L;5d} \chi_{L;5d} b_{L;5d} - 4f \end{bmatrix} \begin{bmatrix} C_{L;4f} b_{L;4f} - 5d \\ 1 + N_{L;5d} \chi_{L;5d} b_{L;5d} - 5d \end{bmatrix} \begin{bmatrix} M_{L;4f} \\ M_{L;5d} \end{bmatrix} = \begin{bmatrix} C_{L;4f} H \\ N_{L;5d} \chi_{L;5d} H \end{bmatrix} \] (12)

where \( B_{L;5d} \) is the constant which equals

\[ B_{L;5d} = \frac{4}{3k_B \mu_B^2} \chi_{L;5d} u_{4f} - 5d \left( g_{sd} \right)^2 \] (15)

and

\[ G_L = (g_L - 1)^2 J_L (J_L + 1) \] (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 component 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 \( B_{L;5d} = B_{R;5d} = B_{sd} \), see (15).

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

$$T_C = (1 - x)T_{CL;4f} + xT_{CR;4f} = (1 - x)B_{L;4f}K^2_{L;4f-5d}G_{L} + xB_{R;5d}K^2_{R;4f-5d}G_{R}. \quad (17)$$

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 $K^2_{L;4f-5d} = K^2_{R;4f-5d} = K^2_{4f-5d}$ is constant across the heavy rare-earth series (similarly to results for the exchange interaction parameters for the $Al_2$ system presented in [1]), the Curie temperature formula takes the simplified form

$$T_C = B_{5d}K^2_{4f-5d}[(1 - x)G_1 + xG_2] = B_{5d}K^2_{4f-5d}G = BG. \quad (18)$$

Here, $G$ is the de Gennes factor, averaged across the rare-earth crystal sublattice and the parameter $B = B_{5d}K^2_{4f-5d}$, 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 $K_{4f-5d}$ 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 $(L/R)Al_2$

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 $Al_2$ compounds. The $Al_2$ 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, 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 $\chi_{5d}$ (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 or considering different members of the rare earth–aluminium series. 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].

Acknowledgments

This research was partially supported by the Rzeszów University of Technology, grant No. UPB.FE.20.001.

References

[1] K.N.R. Taylor, Adv. Phys. 20, 551 (1971).
[2] K.H.J. Buschow, in: Ferromagnetic Materials, Ed. E.P. Wohlfarth, Vol. 1, North-Holland, Amsterdam 1980, p. 297.

[3] E.C. Stoner, Proc. R. Soc. A 165, 372 (1938).
[4] J.F. Janak, Phys. Rev. B 16, 255 (1977).
[5] E. Burzo, L. Chioncel, J. Opt. Adv. Mater. 6, 917 (2004).
[6] B. Gicaha, J. Pszczoła, Z. Kucharski, J. Suwalski, Phys. Lett. A 185, 491 (1994).
[7] F. Laves, Naturwissenschaften 27, 65 (1939) (in German).
[8] I.A. Campbell, J. Phys. F Met. Phys. 2, L47 (1972).
[9] J. Pszczoła, K. Krop, J. Magn. Magn. Mater. 59, 95 (1986).
[10] J. Pszczoła, K. Krop, Acta Phys. Pol. A 76, 247 (1989).
[11] T. Inoue, S.G. Sankar, R.S. Craig, W.E. Wallace, J. Phys. Chem. Solids 38, 487 (1977).
[12] M.A.A. Issa, Ph.D. Thesis, University of Durham, Durham 1973.
[13] K.H.J. Buschow, F.J. Fast, A.M. van Diepen, H.W. de Wijn, Phys. Status Solidi 24, 715 (1967).
[14] J. Heimann, K. Kaczmarska, K. Kaczmarska, E. Kwapułińska, A. Słobarski, A. Chełkowski, J. Magn. Magn. Mater. 27, 187 (1982).
[15] E. Gratz, R. Grössinger, H. Oesterreicher, F.T. Parker, Phys. Rev. B 23, 2542 (1981).
[16] M. Khan, A.K. Pathak, Y. Mudryk, K.A. Gschneidner Jr, V.K. Pecharsky, J. Mater. Chem. C 5, 896 (2017).
[17] Thân-Trong Nguyên, L.B. Chiu, P.R. Elliston, A.M. Stewart, K.N.R. Taylor, J. Phys. F Met. Phys. 6, 1399 (1976).
[18] A.M. Tishin, Y.I. Spichkin, The Magnetocaloric Effect and Its Applications, CRC Press, 2016.
[19] M. Khan, Y. Mudryk, K.A. Gschneidner, Jr., V.K. Pecharsky, Phys. Rev. B 84, 214437 (2011).
[20] M. Khan, K.A. Gschneidner, Jr., V.K. Pecharsky, Phys. Rev. B 80, 224408 (2009).
[21] K.A. Gschneidner, V.K. Pecharsky, S.K. Malik, in: Advances in Cryogenic Engineering, Ed. L.T. Summers, Plenum, New York 1996.
[22] C. Zener, Phys. Rev. 81, 440 (1951).
[23] S.W. Wonsowskij, Magnetizm, Nauka, Moscow 1971 (in Russian).
[24] S. Legvold, in: Ref. [2], p. 183.
[25] P.G. de Gennes, J. Phys. Radium 23, 510 (1962) (in French).
[26] B.N. Harmon, A.J. Freeman, Phys. Rev. B 10, 1979 (1974).
[27] A.J. Freeman, R.E. Watson, *Phys. Rev.* **127**, 2058 (1962).
[28] M. Szklarska-Łukasik, Ph.D. Thesis, AGH, Kraków, 2015 (in Polish).
[29] E. Burzo, L. Chioncel, R. Tetean, O. Isnard, *J. Phys. Condens. Matter* **23**, 026001 (2011).
[30] J.S. Smart, *Effective Field Theories of Magnetism*, Saunders, Philadelphia 1966.
[31] D. Bloch, D.M. Edwards, M. Shimizu, J. Voiron, *J. Phys. F Met. Phys.* **5**, 1217 (1975).
[32] G.J. Bowden, R.K. Day, *J. Phys. F Met. Phys.* **8**, 533 (1978).
[33] A.K. Pathak, C.M. Bonilla, D. Paudyal, Y. Mudryk, V.K. Pecharsky, *J. Alloys Compd.* **774**, 321 (2019).