ISSN 1318-0010
KZLTET 32(6)513(1998)

CALCULATION OF THE CURIE TEMPERATURE IN THE SYSTEM $Nd_2Fe_{17-x}Al_x$

IZRAČUN CURIEJEVE TEMPERATURE V SISTEMU $Nd_2Fe_{17-x}Al_x$

MATEJ KOMELJ, S. KOBE

Jozef Stefan Institute, Jamova 39, 1000 Ljubljana

Prejem rokopisa - received: 1998-11-16; sprejem za objavo - accepted for publication: 1998-12-07

The ferromagnetic alloy Nd_2Fe_{17} has a low Curie temperature (≈330K). By substituting some of the Fe atoms in the crystal lattice with Al atoms the volume of the unit cell is increased and consequently, the Curie temperature increases up to a maximum of ≈470K. Therefore the alloy $Nd_2Fe_{17-x}Al_x$ is potentially suitable as a permanent magnet material. From the electronic structure we have predicted the relative changes of the Curie temperature in the spin fluctuation approximation. We have calculated the electronic structure within the framework of the Density Functional Theory and the Local Spin Density Approximation using the LMTO method.

Key words: permanent magnet materials, Curie temperature, density functional theory

Feromagnetna zlitina Nd_2Fe_{17} ima nizko Curiejevo temperaturo (≈330K). Z zamenjavo nekaterih atomov Fe v kristalni mreži z atomi Al se poveča prostornina osnovne celice in zato tudi Curiejeva temperatura do največ ≈470K. To pomeni, da je zlitina $Nd_2Fe_{17-x}Al_x$ potencialno primerna kot material za izdelavo trajnih magnetov. Iz elektronske strukture smo v okviru približka spinskih fluktuacij napovedali relativne spremembe Curiejeve temperature zaradi prisotnosti Al. Elektronsko strukturo smo izračunali v okviru teorije gostotnih funkcionalov in približka lokalne spinske gostote z uporabo metode LMTO.

Ključne besede: trajno-magnetni materiali, Curiejeva temperatura, teorija gostotnih funkcionalov

1 INTRODUCTION

The R_2Fe_{17} rare- earth intermetallic compounds are, despite their uniaxial magneto- crystalline anisotropy, not suited for permanent magnet materials because of their low Curie temperature (T_C). The first efforts to overcome this problem involved attempts to interstitially modify the basic alloys by introducing carbon[1] or nitrogen[2] into the material. The unit cell volumes of carbided $R_2Fe_{17}C_x$ or nitrided $R_2Fe_{17}N_x$ material are expanded by approximately 5% to 7% and, as a result, their Curie temperatures increase by about 400°C. However, the presence of carbon or nitrogen causes difficulties in the manufacture of these new materials[3]. Hence alternative ways of increasing the volumes of the unit cell and Curie temperatures must be found. One approach is the formation of pseudobinary alloys of the type $R_2Fe_{17-x}M_x$ where M stands for aluminum, silicon or gallium[4].

An example is the alloy Nd_2Fe_{17} with $T_C \approx 330$K i.e. slightly above the room temperature, which enables the use of the material for limited practical applications. G. J. Long et al.[5] experimentally obtained the dependence of T_C on the aluminum content in the system $Nd_2Fe_{17-x}Al_x$. The best improvement ($T_C \approx 470$) was achieved for the alloy with $x \approx 4$.

We have calculated the Curie temperatures of $Nd_2Fe_{17-x}Al_x$ relative to the T_C of Nd_2Fe_{17}.

2 THEORY

The only reliable theoretical investigations of magnetic properties of the crystalline materials are based on calculation of the electronic structure from first principles within the framework of the density functional theory[6]. This theory is valid only for the description of the electronic ground state of the crystal which is in reality present only at zero temperature. Therefore the Curie temperature can not be derived rigorously without using any approximations. The easiest approach follows the Stoner theory of ferromagnetism from 1936[7]. It is based on the idea that above the Curie temperature not just the exchange interaction but also particular local magnetic moments disappear. This is not true because in the paramagnetic state the local magnetic moments are still present but they are randomly oriented due to thermal excitations. However the Stoner Curie temperature (T_S) serves as the starting point for better approximations. The next step was undertaken by Mohn and Wohlfarth[8] who considered also the effects of spin fluctuations. They introduced the characteristic temperature T_{TS} describing the influence of spin fluctuations. The approximate Curie temperature T_C is the solution of the equation:

$$\frac{T_C^2}{T_S^2} + \frac{T_C}{T_{SF}} - 1 = 0. \qquad (1)$$

Both quantities, T_S and T_{SF} are obtained from the electronic structure. We have calculated it using the linear-muffin-tin-orbital (LMTO) method[9] in the atomic-sphere (ASA) approximation. Another simplification must be performed to describe the exchange- correlation potential between electrons. We have chosen the most common way applying the local spin density approximation (LSDA)[10].

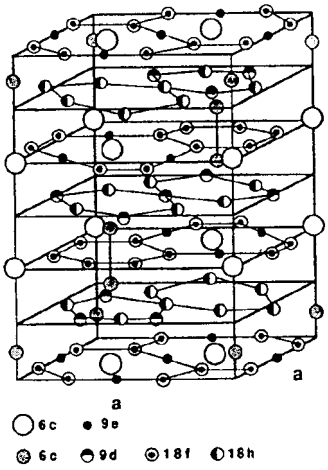

Figure 1: Rhombohedral crystall structure of $Nd_2Fe_{17-x}Al_x$
Slika 1: Romboedricna kristalna struktura $Nd_2Fe_{17-x}Al_x$

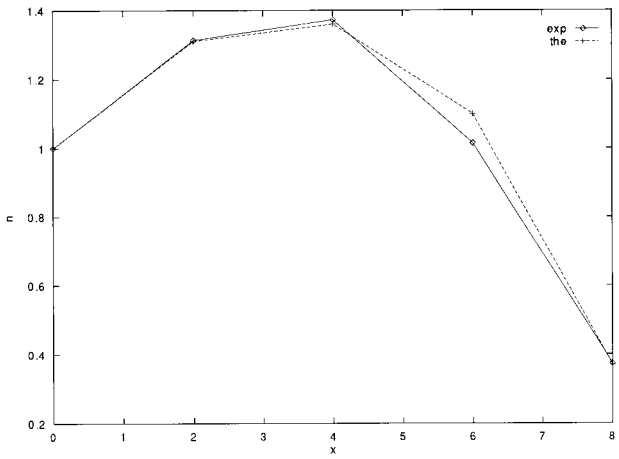

Figure 2: Comparison between theoretically and experimentally[5] determined ratio n = $T_C(Nd_2Fe_{17-x}Al_x)/T_C(Nd_2Fe_{17})$ as a function of aluminum content x
Slika 2: Primerjava med teoretično in eksperimentalno določenim razmerjem n = $T_C(Nd_2Fe_{17-x}Al_x)/T_C(Nd_2Fe_{17})$, kot funkcijo vsebnosti aluminija x

3 RESULTS

All the calculations for the system $Nd_2Fe_{17-x}Al_x$ have been performed using experimentally obtained values[3] of the lattice constants. The Nd_2Fe_{17} compound crystallizes in the rhombohedral Th_2Zn_{17} type structure which is shown on **Figure 1**. On the basis of neutron diffraction experiments[5] it was found that Al atoms substituted Fe atoms in the crystal lattice of the system $Nd_2Fe_{17-x}Al_x$, however the aluminum almost completely avoids the 9d site. At compositions up to an x of approximately 6, aluminum prefers the 18h site and occupies the 6c and 18f sites in an approximately random mode. In contrast, at higher aluminum compositions, aluminum strongly prefers the 6c and 18f sites and the aluminum occupancy of the 18h site remains relatively constant at approximately 45%. Since the calculations are limited to the completely periodic structures we have supposed the models for unit cells where the positions of Al atoms were fixed.

We have realized, as demonstrated previously (see for example[11]), that the Mohn Wohlfarth theory in connection with LSDA does not give the right values for T_C, but the relative changes agree well with the experimental results. This is evident from **Figure 2** where the ratio $T_C(Nd_2Fe_{17-x}Al_x)/T_C(Nd_2Fe_{17})$ is plotted against the aluminum content x. The agreement between theory and experiment[5] is the worst for x=4 and 6. This can be explained by the fact that compounds with such aluminum contents in reality do not exhibit long range order and can not be described just by one unit cell. The Curie temperature of $Nd_2Fe_9Al_8$ is almost three times lower than the T_C of the basic alloy because the material exhibits just weak ferromagnetism due to the low Fe content.

4 CONCLUSION

We have carried out the band structure calculations for the system $Nd_2Fe_{17-x}Al_x$ using the LMTO ASA[9] which is suitable for the investigations of the properties of ideal crystals. The compounds with $x \neq 0$ do not have a real periodic structure. Our results could be improved by taking into account more than just one unit cell but this would require enormous computational time.

The Mohn Wohlfarth theory[8] considers Stoner excitations and spin fluctuations which both destroy magnetization of a ferromagnetic material. A more reliable approach should also include magnons although the use of LSDA[10] is the main reason why only the relative changes and not the T_C itself can be predicted. The only proper way to theoretically determine Curie temperature would be a real temperature dependent band structure calculation. So far this still remains a challenge for solid state physics.

5 REFERENCES

[1] D. B. de Mooij, K. H. J. Buschow, *J. Less-Common Met.*, 142 (1988) 349
[2] J. M. D. Coey, H. Sun, *J. Magn. Magn. Mater.*, 87 (1990) L251
[3] K. H. J., *in Supermagnets, Hard Magnetic Materials*, edited by G. J. Long, F. Grandjean (Kluwer, Dordrecht, 1991) p. 553
[4] F. Weitzer, K. Hiebl, P. Rogl, *J. Appl. Phys.* 65 (1989) 4963
[5] G. J. Long, G. K. Marasinghe, S. Mishra, O. A. Pringle, Z. Hu, W. B. Yelon, D. P. Middleton, K. H. J. Buschow, F. Grandjean, *J. Appl. Phys.* 76 (1994) 5383
[6] P. Hohenberg, W. Kohn, *Phys. Rev.*, 136 (1964) B864
[7] E. C. Stoner, *Proc. Royal Soc. A*, 154 (1936) 656
[8] P. Mohn, E. P. Wohlfarth, *J. Phys. F: Met. Phys.*, 17 (1987) 2421
[9] O. K. Andersen, *Phys. Rev. B*, 12 (1975) 3060
[10] W. Kohn, L. J. Sham, *Phys. Rev.*, 140 (1965) A1133
[11] Q. Qi, R. Skomski, J. M. D. Coey, *J. Phys.: Condens. Matter*, 6 (1994) 3245