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Magnetic ordering schemes in $R_3T_4X_4$ compounds

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This work is an attempt to systematize the magnetic structures of $R_3T_4X_4$ (R – rare earth atom, T – transition metal, X – p-electron element) compounds, investigated by neutron diffraction in the course of a broader research programme. Experiments were performed for twenty samples containing Pr, Nd, Tb, Dy, Ho, and Er. Although the determined structures display a huge variety, some regularities were found. Different approaches are tried in order to elucidate the observed behaviours, and several conclusions are arrived at concerning the factors responsible for the observed magnetic ordering schemes.

Key words: *magnetic ordering; rare earth intermetallics; neutron diffraction*

1. Introduction

The research reported here aims at performing a detailed study of isostructural 3:4:4 compounds crystallizing in the $Gd_3Cu_4Ge_4$-type structure (space group *Immm*), expected to bring a systematisation in their magnetic properties, including magnetic structures. The most interesting feature of these intermetallics is the fact that rare earth ions occupy two symmetry non-equivalent positions (4e and 2d).

Twenty three compounds such as $R_3Mn_4Sn_4$ (R = La, Pr, Nd), $R_3Cu_4Si_4$ (R = Tb, Dy, Ho, Er), $R_3Cu_4Ge_4$ (R = Nd, Tb, Dy, Ho, Er), $R_3Cu_4Sn_4$ (R = Pr, Nd, Tb, Dy, Ho, Er), $R_3Pd_4Ge_4$ (R = Tb, Ho, Er), and $R_3Ag_4Sn_4$ (R = Pr, Nd) have been investigated by means of neutron powder diffraction. The determined magnetic structures exhibit a huge diversity, however some regularities were found.

2. Experimental results and discussion

The samples were synthesized and examined as described elsewhere [1], where a detailed description of the determined magnetic structures can also be found. Mag-

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netic data indicate that all the investigated compounds are antiferromagnets at low temperatures. The whole group may be divided into three sub-groups: manganese compounds, light rare earth compounds, and heavy rare earth compounds, which will be described below.

In the compounds containing manganese, i.e. $R_3Mn_4Sn_4$ (R = La, Pr, Nd), the manganese moments are the first to order on decreasing temperature. In the La compounds, they are actually the only ones that do order, forming a sine-wave modulated structure described by the propagation vector $\mathbf{k} = (k_x, 0, 0)$, with magnetic moments always lying in the *bc* plane. The value of k_x increases with temperature. In the Pr and Nd compounds, the rare earth magnetic moments at the 4e sites order as well, in both cases forming collinear structures described by the propagation vector $\mathbf{k} = (1, 1, 1)$; their ordering temperatures, however, are lower than the ordering temperatures of the Mn sublattices. The magnetic moments of Pr and Nd lay in the *ab* planes for both compounds.

The Néel temperatures corresponding to the Mn sublattice ordering decrease with the increasing Z value of the R element, which corresponds to a decreasing unit cell volume. This is an anomalous result. The Néel temperatures for the rare earth sublattices fulfil the de Gennes relation. The ratio $T_N(\mathrm{Nd})/T_N(\mathrm{Pr})$ is equal to 2.4, whereas the corresponding ratio of de Gennes factors is 2.3.

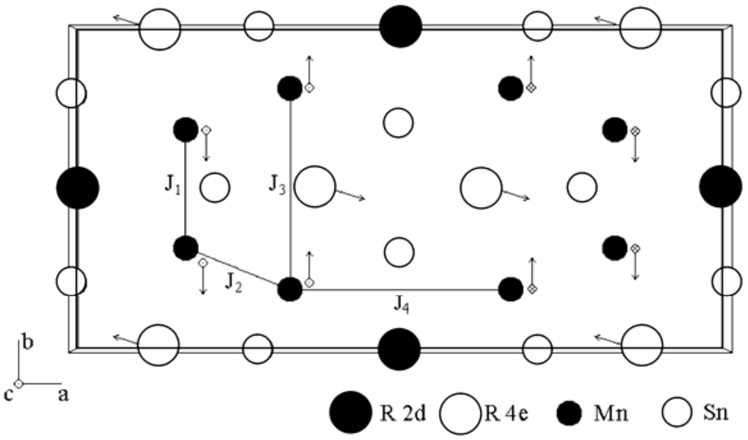

Fig. 1. Crystal structure of the $R_3Mn_4Sn_4$ (R = La, Pr, Nd) compounds projected along [001], with four different exchange integrals among the Mn magnetic moments. The vectors show the components of the Mn magnetic moments and the directions of the rare earth magnetic moments in the Pr and Nd compounds

The interaction between Mn moments may be described by four integrals, J_1, J_2, J_3, and J_4 (Fig. 1), related to four Mn–Mn interatomic distances, d_1, d_2, d_3, and d_4, respectively. The shortest distance, d_1 (smaller than 2.88 Å), corresponds to the ferromagnetic coupling between moments ($J_1 > 0$). The other distances are larger than

3.21 Å. In $La_3Mn_4Sn_4$, all the other integrals are also positive. In the case of $Pr_3Mn_4Sn_4$ and $Nd_3Mn_4Sn_4$, only J_2 is negative, whereas the other two integrals are positive as well. The idea of a critical Mn–Mn distance of about 2.85 Å, which would govern interionic coupling, applicable to many manganese-transition metal alloys and proposed by Goodenough on the assumption of localised/delocalised 3d electrons [2, 3], does not seem to work in this case.

The dependence of the magnetic moment of Mn on Mn–Mn and Mn–Sn interatomic distances reveals a positive correlation, similar to the one observed for rare earth manganese-germanides [4]. This result indicates a stronger localization of d electrons on manganese atoms. In the Pr and Nd compounds, rare earth magnetic moments in the 4e sublattice become ordered independently on Mn at low temperatures. A similar behaviour is observed in other Pr and Nd compounds [5–7], where the manganese–rare earth interatomic distances are larger than 3 Å, analogously to the compounds studied in this work. These results indicate a weak interaction between the rare earth and manganese sublattices.

The R–Mn coupling is different in various compounds; non-collinear ordering is observed in the majority of cases. Iwata et al. showed that for light rare earths the ferromagnetic coupling between the R and Mn sublattices is dominant [8]. Such a behaviour is observed for $NdMn_2Si_2$ [9]. In other compounds, antiferromagnetic (for example in $PrMnSi_2$ [6]) or complex (NdMnSi, $NdMnSi_2$) coupling is observed, similar to the one appearing in the compounds investigated here. The above results confirm independent magnetic ordering in rare earth sublattices.

In the case of light rare earth compounds, the rare earth magnetic moments were found to order in $Nd_3Cu_4Ge_4$, $Pr_3Cu_4Sn_4$, and $R_3Ag_4Sn_4$ (R = Pr, Nd). The only exception was $Nd_3Cu_4Sn_4$, in which no ordering was detected down to 1.5 K. The predominant arrangements observed in this group are the structures described by the propagation vector $\mathbf{k} = (1, 1, 1)$, with magnetic moments pointing along the a-axis or laying in the a-b plane. Only in $Nd_3Cu_4Ge_4$ do the magnetic moments point along the c-axis, and simultaneously only in this case the 2d sublattice does not order.

The Néel temperatures of the light rare earth compounds do not fulfil the de Gennes relation. The experimental values are larger than those resulting from de Gennes scaling normalized to the Néel temperatures of isostructural $Gd_3T_4X_4$ compounds. The values of $\Delta T_N = T_{N\mathrm{obs}} - T_{N\mathrm{calc}}$ ($T_{N\mathrm{calc}}$ is determined as T_N normalized to the Néel temperature of the isostructural Gd compound) decrease with an increasing number of the 4f electrons. These differences between the observed and calculated values result from the strong influence of the crystalline electric field effect [10] or hybridisation of 4f shells with conduction bands and/or d or p shells of the surrounding atoms [11].

The largest group, in which the magnetic structures were determined, are heavy rare earth compounds, i.e. $R_3Cu_4Si_4$ (R = Tb, Dy, Ho, Er), $R_3Cu_4Ge_4$ (R = Tb, Dy, Ho, Er), $R_3Cu_4Sn_4$ (R = Tb, Dy, Ho, Er), and $R_3Pd_4Ge_4$ (R = Tb, Ho, Er), which simultaneously display the largest diversity. Both rare earth sublattices become ordered in all of them. The most distinctive feature in this group is the existence of more than one critical temperature (observed for 12 out of 15 compounds) which indicates changes in magnetic structure with temperature. These changes concern disordering of one of the two rare earth sublattices or involve a transformation of the propagation vector.

The most frequently observed arrangements in this group are the structures described by the vector **k** = (0, 1/2, 0) or its derivatives **k** = (0, 1/2 +δ, 0), where $\delta < 0.03$ (in 9 cases out of 15). These structures often coexist with other, modulated arrangements at low temperatures (in 7 cases out of 9). The described ordering type dominates in $R_3Cu_4Si_4$ and $R_3Cu_4Ge_4$ compounds (it appears in all the studied compounds, in fact).

Among the $R_3Cu_4Sn_4$ compounds, two (R = Tb, Dy) have structures described by the propagation vector **k** = (0, 0, 1/2 + δ), where $\delta < 0.09$, which do not change with temperature. For one compound (R = Er), the propagation vector **k** = (1/2, 1/2, 0) is accompanied by another one at low temperatures, and one compound (R = Ho) has a very complex structure that changes with temperature, described by different sets of vectors in each range.

Regarding the $R_3Pd_4Ge_4$ compounds, all of them have modulated structures described by propagation vectors with two (R = Tb, Ho) or one (R = Er) non-zero components. These propagation vectors in two cases (R = Tb, Er) are accompanied by the propagation vector **k** = (0, 0, 0) at low temperatures.

The reported changes in the propagation vectors, connected with transitions from commensurate structures at low temperatures to modulated, non-commensurate ones in the vicinity of the Néel temperature, are very common among rare earth intermetallics. They may be explained as a result of temperature-dependent free energy for different propagation vectors appearing in the presence of magnetocrystalline anisotropy [12, 13].

The other analysed parameter is the direction of the magnetic moment which may provide information about magnetocrystalline anisotropy and crystalline electric field parameters. Among light rare earth compounds (Pr, Nd), rare earth magnetic moments in the 2d sublattice are parallel to the *a*-axis, which in general applies to the 4e sublattice magnetic moments as well (except for $Nd_3Cu_4Ge_4$ and $Nd_3Ag_4Ge_4$). It is much more difficult to find any distinct trends among the heavy rare earth compounds (Tb–Er). In the $Tb_3Cu_4X_4$ (X = Si, Ge, Sn) series, the Tb 2d magnetic moments are parallel to the *a*-axis, in the $Ho_3Cu_4X_4$ (X = Si, Ge, Sn) compounds the Ho 2d moments are parallel to the *b*-axis, and in $Er_3Cu_4X_4$ (X = Si, Ge, Sn) and $Er_3Pd_4Ge_4$ the Er 2d moments are parallel to the c-axis. Finding the respective regularities for the 4e sublattice is impossible.

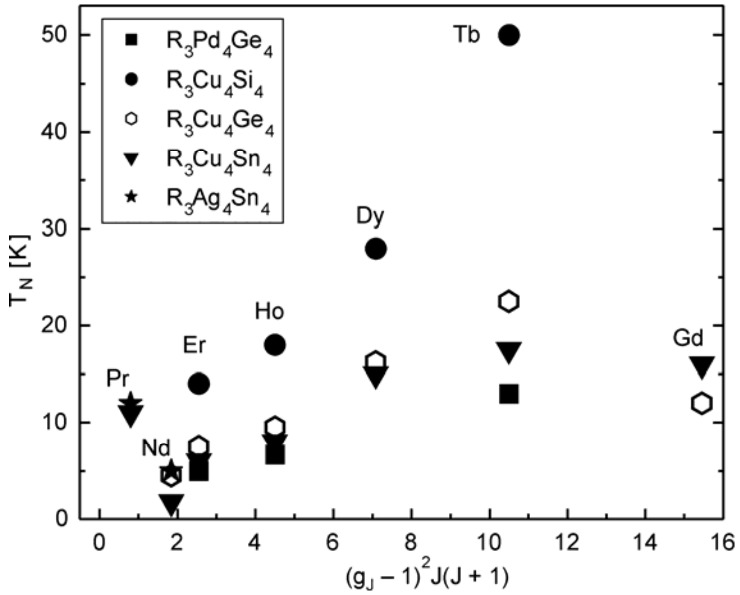

Fig. 2. Néel temperatures of $R_3Ag_4Sn_4$ (R = Pr, Nd), $R_3Cu_4Si_4$ (R = Tb, Dy, Ho, Er), $R_3Cu_4Ge_4$ (R = Nd, Tb, Dy, Ho, Er), $R_3Cu_4Sn_4$ (R = Pr, Nd, Tb, Dy, Ho, Er), and $R_3Pd_4Ge_4$ (R = Tb, Ho, Er) versus the de Gennes factor. The Néel temperatures of $Gd_3Cu_4Sn_4$ and $Gd_3Cu_4Ge_4$ were taken from [9] and [11], respectively

It is commonly known that the observed magnetic ordering results from exchange interaction transferred via conduction band electrons, as described by the RKKY model. Its adoption here is justified by large spacing between rare earth moments and the fact that the investigated compounds are good conductors [14]. According to this model, the critical temperatures connected with magnetic ordering should be proportional to the above-mentioned de Gennes function, $(g_J - 1)^2 J(J + 1)$ [15, 16]. For the compounds discussed here, this scaling is not fulfilled (Fig. 2), which suggests that additional factors are responsible for the ordering that appears. The first factor that needs to be considered is the influence of the crystalline electric field [10].

The description of the RKKY-type interaction is connected with the interaction integral $J(X)$, which is an oscillatory function of $X = k_F R_{ij}$ ($F(X) = (X\cos X - \sin X)X^{-4}$), where k_F is the Fermi vector and R_{ij} is the distance between the ith and the jth spin. In order to enable an interpretation of the obtained results, the Fermi vector must be calculated. For $Tb_3Cu_4Si_4$, it was evaluated to be 1.672 Å^{-1}. Taking into account the distances between a singled out Tb atom in the 4e sublattice and the nearest Tb atoms in the 2d sublattice of this compound (equal to 3.663, 5.039 and 5.516 Å), one obtains the following values of the product $k_F R_{ij}$: 6.120, 8.425 and 9.223. Two of these numbers are close to the zero points of the oscillatory function $F(X)$, equal to 6.425 and 9.530. This result indicates that the interactions originating from the magnetic moments in the 2d sublattice almost cancel out at the 4e sites and the magnetic moments in this sublattice are ordered independently in consequence. The same explanation can be applied for the other $R_3Cu_4X_4$ (X = Si, Ge, Sn) compounds for the sake of the similarity of their (also electronic) structures. Magnetic ordering in two symmetry non-equivalent sublattices also proceeds independently in many of the $RTGe_2$ compounds (T = Pt, Pd, Ir) [17–19].

The ^{166}Er Mössbauer spectroscopy performed for $Er_3Cu_4X_4$ (X = Si, Ge, Sn) at different temperatures [20] shows that the effective field in the 2d sublattice is larger than in the 4e sublattice, which suggests that a similar relation should appear in the case of magnetic moments. For $Er_3Cu_4Si_4$, a line broadening referring to the 4e sublattice is observed in the spectrum obtained at 2 K, which can be ascribed to the existence of magnetic moment relaxation in this sublattice. Neutron diffraction measurements carried out for this compound reveal a broadening of the magnetic reflexes connected to diffraction on Er magnetic moments in the 4e sublattice, which indicates that the correlation length is of the order of 20 Å [20]. The cited experimental facts suggest that the ordering in the 4e sublattice is induced by the moments in the 2d sublattice.

For $R_3Cu_4X_4$, a distinct regularity is observed: $T_N(X = Si) > T_N(X = Ge) > T_N(X = Sn)$. Additionally, the transition temperatures of the copper compounds are higher than those of the palladium compounds. As already mentioned above, the local symmetries and atomic surroundings of the rare earth atoms occupying two different sublattices differ from each other. In order to investigate the influence of these factors on the crystalline electric field parameters, calculations based on the point charge approximation (described in detail in [1]) were performed for some of the investigated compounds, namely $R_3Cu_4Sn_4$ (R = Pr, Nd, Tb, Dy, Ho, Er), $Tb_3Cu_4X_4$ (X = Si, Ge, Sn), and $Tb_3Pd_4Ge_4$. It must be clearly stated that the applied method, though very simple, can give only scarce information on the real values of the B_n^m parameters and should rather be treated as the one that gives a very raw estimation.

Concerning copper stannides, while passing from holmium to erbium, the signs of the crystalline electric field parameters change, due to a change in the sign of the Stevens α parameter. The second important result following from these calculations is the observation that the three parameters B_2^0, B_2^2 and B_4^0 are of a comparable magnitude, which suggests that their participation in the formation of a magnetic structure is evenly important. It seems that for these compounds the complete crystalline electric field Hamiltonian needs to be considered, which contradicts the case of, for example, the RT_4X_4 series [10], for which magnetic structure formation is determined solely by B_2^0. The calculations aiming at revealing the possible influence of d- or p-electron elements (those performed for $Tb_3Cu_4X_4$ (X = Si, Ge, Sn) and $Tb_3Pd_4Ge_4$) did not reveal any evident relationships.

3. Conclusions

It seems that at this stage it is not possible to unambiguously point out one factor, or even a set of factors, to which any vital, decisive role in the formation of a magnetic structure can be ascribed. It appears that only further and broader studies of compounds of this class may yield premises for elaborating a suitable theory or at least for finding some explicit, general regularities.

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