Correlation between Atomic Spacing and Magnetic Behaviour in Ce Binary Compounds

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Abstract

The magnetic behaviour of 80 Ce-binary compounds is correlated with the minimum Ce-Ce spacing (D) in the lattice. Among the magnetically ordered compounds, three regions can be defined: I) with D smaller than the trivalent Ce diameter, where all the compounds order antiferromagnetically, with fractional entropy and large values of γ and θ_p. II) With 3.7Å < D < 4.1Å, which includes the ferromagnetic compounds, and III) with D >4.1Å, where most of the compounds order antiferromagnetically with full entropy.

The compounds which do not order magnetically (region IV) are distributed in two ranges of energy: <10K for the Heavy Fermions and >100K for the Intermediate Valent ones. Spin Fluctuation effects are observed in the compounds with large D values and small volume contraction.

Keywords: Magnetic Order, Heavy Fermions, Intermediate Valence, Spin Fluctuations.

Introduction

Cerium presents a large variety of physical phenomena as a pure metal (1) or within an intermetallic compound (2), due to the vicinity of the energy of its "inner" $4f^1$ shell to the "outer" 5d and 6s levels.

About 150 Cerium binary compounds are reported at present with recognized crystalline structure, see for example the "Pearson's Handbook" (2). Among them, about eighty have a known magnetic behaviour, and are gathered following their dominant magnetic characteristics, as for example Ferro or Antiferromagnets (those which order magnetically) and Heavy Fermions, Kondo-lattices or Intermediate Valent (when they do not order magnetically). However, at present the amount of experimental data give the chance to attempt to compare these different groups through phenomenological parameters, allowing to extract properties and behaviours which are not accounted for the specific microscopical models.

The parameters to be used for such analysis have to be unique (independent of the models) and universal (observable in all the compounds). We propose for this goal the characteristic magnetic temperature (T_o) and the Ce-Ce interatomic spacing (D) . The value of T_o is taken from the ordering temperature, T_C or T_N, or from the temperature of the maximum of the susceptibility, T_M, for those which do not order magnetically. The second parameter is taken from the minimum Ce-Ce distance, in the lattice. A former attempt to this kind of analysis was done by Hill (3), on seventeen Ce compounds known at that time.

We shall see that there is a number of Ce compounds where the Ce atom have unequivalent positions in the lattice. In those

cases, each Ce sub-lattice may show different magnetic behaviour because of their different environments. For simplicity, we will identify each compound by its highest ordering temperature and the minimum Ce-Ce spacing. Although the minimum D value should correlate with the maximum T_C or T_N when the magnetic ion is stable valent, that is not guaranteed in the case of Ce because of its ability in changing its valence under certain environmental conditions.

In fig. 1 we plot the transition temperatures of those Ce compounds which order magnetically versus the minimum Ce-Ce distances. There, a generic compound Ce_jX_k is labeled as $_jX_k$. Concerning the distribution of the Ferromagnetic (FM) and Antiferromagnetic (AFM) compounds, it becomes evident that they are not randomly distributed, on the contrary, the FM ones are concentrated in the 4.1>D>3.7Å range. Considering that some physical reason underlies in such distribution, we will subdivide fig. 1 in three regions: I) with D < 3.7Å, II) with D ranging between 4.1 and 3.7Å and III) with D > 4.1Å. The first boundary (between regions I and II) can be immediately associated with the diameter of a trivalent Ce atom (1), as indicated by the β and γ phases of metallic Ce. In other words, at such a D value two trivalent Ce rigid spheres are expected to touch each other. The second boundary (between regions II and III) is arbitrarily taken right above the FM compounds with the largest D value.

These boundaries are explicitly shown in fig. 2. There we represent these compounds according to their respective magnetic behaviours. The Ferromagnets are represented by squares, the Antiferromagnets by circles and the diamonds are used for those compounds showing more than one magnetic transition. The last

case is mainly observed in the compounds having unequivalent positions of the Ce atoms in the lattice, suggesting that each Ce-sublattice behaves independently. Note that Ce compounds in which one of the sublattices does not order magnetically are also reported in the literature (4). Also in fig. 2, we include information on the entropy gain related with the magnetic transition. The symbols crossed once (twice) have fractional (full) entropy gain at the transition. In thecases which, no information is available, open symbols are used.

Finally, the compounds with a non magnetic ground state, which we will consider as belonging to a region IV, are shown in fig. 3, including also metallic Ce in its α phase. Here the characteristic temperature, T_M, is taken from the temperature of the maximum of the magnetic susceptibility. They are spread over a large range of D: between 3.1 and 5.2Å.

We will discuss now the main common features of the compounds belonging to each region. For such a purpose, we have at first to define some parameters of reference. With a few exceptions (which occur in cubic symmetries), the expected entropy gain at the magnetic transition for a Ce magnetic atom is $\Delta S = R\ell n2$, which corresponds to a doublet crystal field ground state. Then, the terms "fractional" or "full entropy" will be used in reference to the value $R\ell n2$. Concerning the temperature dependence of the specific heat, C_p, most of the intermetallic compounds show a linear contribution to the specific heat, C_p, at a certain range of temperature. Although such behaviour has an electronic origin, a linearity in temperature does not represent necessarily a density of states as the Sommerfeld term, γT, does. It is, however, very illustrative to compare the C_p/T ratio of related

compounds. Then, we define γ_{LT} and γ_{HT} as C_p/T at $T < T_o/2$ and $T > 2T_o$ respectively, being T_o the characteristic temperature of the system: T_C, T_N or T_M.

We will discuss now the main characteristics of the compounds belonging to each region.

Region I: compounds with small Ce-Ce spacing

The compounds belonging to the region I ($D < 3.7$Å) show a great variety of crystalline structures, which makes a strict comparison of their properties quite difficult. Nevertheless, by taking as a "general rule" the one which applies to a 90% of the cases, some distinctive characteristics can be attributed to these compounds. They are: i) all order as AFM or show more than one magnetic transition when they have unequivalent positions for the Ce atom, ii) where measured, the entropy gain at T_N is significatively smaller than the expected $R\ell n2$ value. In the best of cases ΔS reaches 90% of that value at $T \sim 3T_N$. iii) The parameters γ_{LT} and γ_{HT} are about one order of magnitude larger than the γ term observed in the non-magnetic reference compounds. iv) The Curie-Weiss temperature, θ_p, is negative and $|\theta_p|$ more than one order of magnitude larger than T_N, alsmot in one crystallographic direction. v) There is no appreciable volume contraction, with respect to the neighbouring Lanthanide (La and Pr) iso-compounds is observed. vi) With few exceptions their crystalline structure has low symmetry (lower than cubic), making their physical properties strongly anisotropic and the number of Ce nearest neighbours is ten or less. All these properties reflect the fact that, although a volume contraction is not detected, there is a significative hybridization of the 4f Cerium orbitals in all these compounds.

With the exception of Ce_3Al_{11} and $Ce_{24}Co_{11}$, all the compounds where the Ce atom has two or more unequivalent positions in the lattice, belong to this region. The coexistence of different magnetic behaviour is reflected in more than one magnetic transition, as in Ce_5Rh_3 and Ce_7Rh_3 (4), or in a transition followed by other anomalies in the specific heat, as in Ce_5Si_3(5).

Region II: Ferromagnetic Compounds

This region, with $4.1 > D > 3.7$ (see figs. 1 and 2), is characterized for including the FM compounds. Although in this region there are also some AFM compounds, practically all of them are related by structure to the ferromagnets. In order to make a comparison between these compounds and those of region I, we resume the general characteristics of this group as follows: i) Practically all the Ce-FM are included in this region, having equivalent Ce positions in the lattice. ii) Most of the compounds reach the expected $R\ell n2$ entropy value at or right above the ordering temperature. iii) The measured γ_{LT} and γ_{HT} values are significatively smaller than in region I. iv) The same reduction is observed in $|\theta_p|$. v) There is no appreciable volume contraction. vi) There are no Ce-FM with cubic structure and those which are cubic at room temperature, undergo a martensitic transformation at $T > T_C$.

The link between the CsCl (bcc) compopunds which order AFM and those which order FM after undergoing a structural transition is given by the pressure effects. Both Ce Zn and Ce Tl order AFM at normal pressure, but a pressure of about 10Kbars induces a Martensitic transformation associated with the appearance of FM order (6-7). The other equiatomic compounds found in this region

have the CrB (CePd and CePt) and the FeB (CeCu, CeSi and CeGe) crystalline structure, see ref. 2. The first group order FM while the second AFM.

Region III: compounds with large Ce-Ce spacing

The compounds with D > 4.1Å belong to this region see also figs. 1 and 2. They have a great variety of magnetic behaviours and crystalline structures. Following the same criterion for describing their properties, we can say that: i) practically all of them order AFM and the pair which presents FM order can be explained as due to frustration effects. ii) Most of the compounds reach the R$\ell n2$ entropy at the transition. The lack of entropy is associated with: iii) large γ_{HT} and iv) large $|\theta_p|$. v) No volume effects are observed and vi) as mentioned before, the structural symmetry is associated with the frustration effects in the compounds showing FM phases.

Due to the large Ce-Ce spacing, the magnetic interaction in this region is expected to be dominated by an RKKY-type mechanism. This fact can be verified in two sets of isostructural compounds, where the Ce-partners have the same electronic structure. They are CeX (X=Te,Se, S and P) and CeX_3 (X=Pb, In and Tl).

The compound $CeGa_2$, which has a FM low temperature phase, confirms the fact that Ferromagnetism should not be expected in this region because, due to his honey-comb structure, it undergoes three AFM transition before becoming FM (8) because of the magnetic frustration effects.

Region IV: Compounds which donot order magnetically

Finally, the compounds which do not order magnetically are

shown in fig. 3. There the energy scale is taken from the temperature of the maximum of the magnetic susceptibility, T_M. It becomes evident from fig. 3 that they are split in two groups: those with $T_M \leq 10K$ (Heavy Fermions) and those with $T_M \geq 100K$ (Intermediate Valent). Their distinctive properties are: i) The Heavy Fermions have a large γ_{LT} value (>400mJ/mole K^2) while the γ_{HT} is about 250mJ/moleK^2. ii) The Intermediate Valent show γ_{LT} within 12 and 100 mJ/moleK^2 and the compounds with large γ_{LT} show effects of spin fluctuations (4). iii) The Intermediate Valent compounds show a significative volume contraction (up to 10% with respect to their Lanthanide neighbours). iv) Most of the Intermediate Valent (IV) compounds have a cubic crystalline structure, with equivalent sites in the lattice.

Although the number of Ce-Heavy Fermion (HF) compounds is growing continuously, noteworthy is the fact that the new systems are ternary compounds. Out of the archetypes of binary HF: $CeAl_3$ and $CeCu_6$, only Ce_3In (9) is the new candidate of the last decade. Usually, a large Ce-Ce spacing is accepted as a condition for a heavy quasiparticle band formation, however Ce_3In, being a Ce concentrated compound with fcc structure, have D values comparable to those of metallic Ce.

The compounds showing Spin Fluctuations (SF) effects are placed among the IV ones when the T_M scale of energy is chosen for comparison. However, if the volume contraction $\Delta V/V \leq 1\%$ (with respect to an hypotetical trivalent compound) is taken into account, then: $CeBe_{13}$, $CeSn_3$, $CeSi_2$ and $CePd_3$ have to be considered within a different kind of behaviour. As mentioned before, the large volume contraction, $\Delta V/V \geq 3\%$, is distinctive of the IV compounds. It can be observed that the largest volume

contrction occurs in the Laves compounds (CeX_2) with four Ce-Ce and twelve Ce-X contacts, which gives the largest number of next-neighbours for the Ce atom (10).

Concerning the few Ce cubic compounds with a quartet (Γ_8) crystalline field ground state, although they belong to different regions, they have as a common feature that they undergo a quadrupolar transition before defining their collective ground state. Within this group we can mention CeZn, CeAg, CeB_6 and Ce_3In (4).

Conclusions

We have seen that new information on the magnetic behaviour of Ce in its binary compounds can be obtained by correlating the characteristic energy of each compound with the Ce-Ce spacing. The most significative conclusions can be resumed as follows: i) the Ce-Ce compression does not necessarily induce valence instability, because cubic local symmetry is required together with a high coordination number, ii) the ferromagnetic behaviour of Ce is also related with local symmetry, iii) the characteristic temperature, T_M, of the compounds which do not order magnetically has two different ranges of values: $T_M < 10K$ for the HF and $T_M > 100K$ for the IV, iv) the SF effects are present in compounds with large D values and low volume contraction[11] and v) the cubic compounds where Ce has a quartet crystalline field ground state undergo a quadrupolar transition at or above its ordering temperature.

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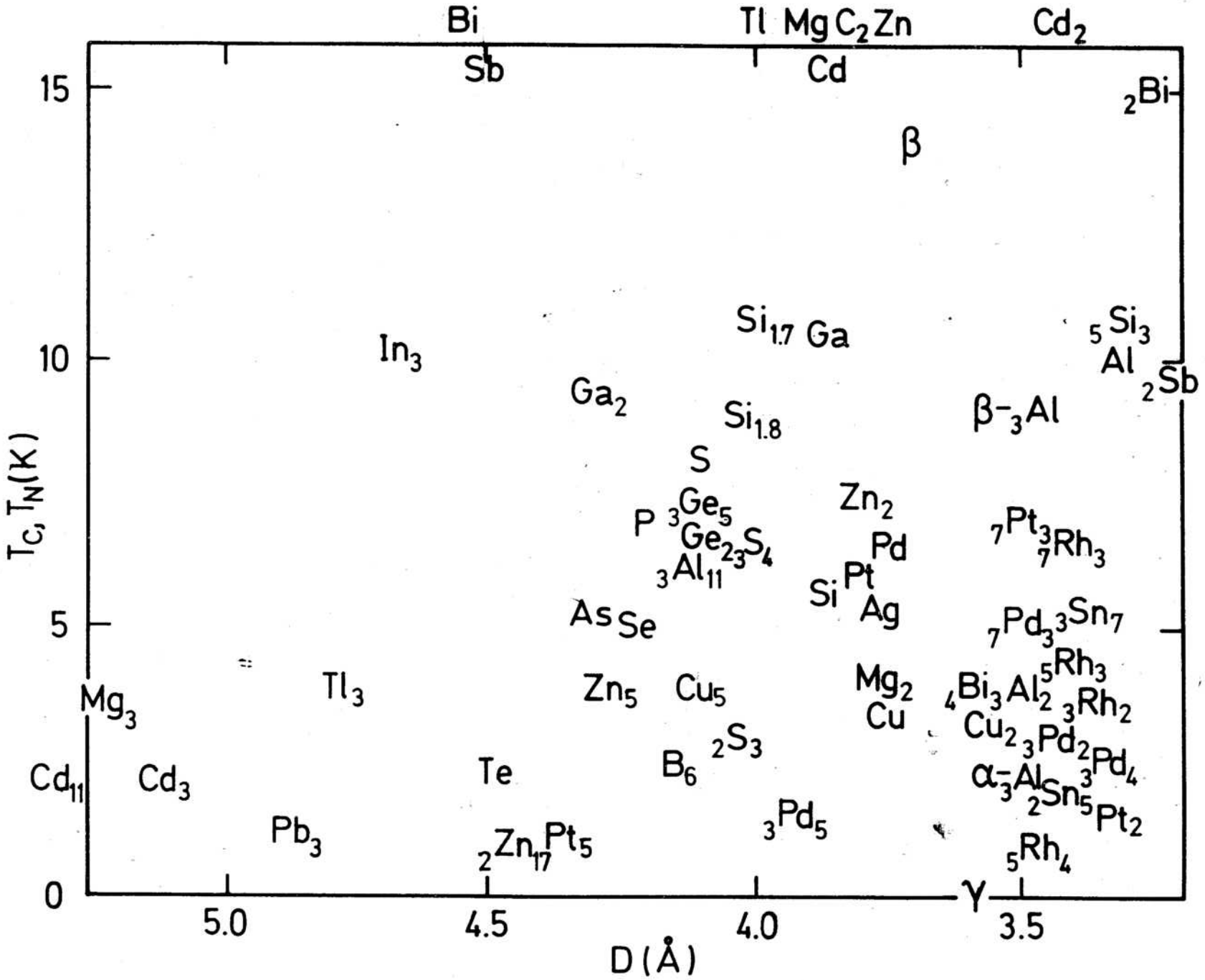
Figure Captions

Fig. 1: Magnetic ordering temperatures of the Ce_jX_k compounds (labeled as $_jX_k$) versus the minimum Ce-Ce spacing. β and γ are the Ce allotropic phases. Dashed lines are the boundaries of the ferromagnetic region.

Fig. 2: Magnetic ordering temperatures versus Ce-Ce spacing. Squares indicate T_C, circles T_N and diamonds identify the compounds with more than one transition. Those crossed once (twice) have fractional (full) entropy gain at the magentic transition.

Fig. 3: Temperature of the maximum of the susceptibility, T_m, of the non-magnetic Ce_jX_k compounds (labeled as $_jX_k$) versus the Ce-Ce spacing.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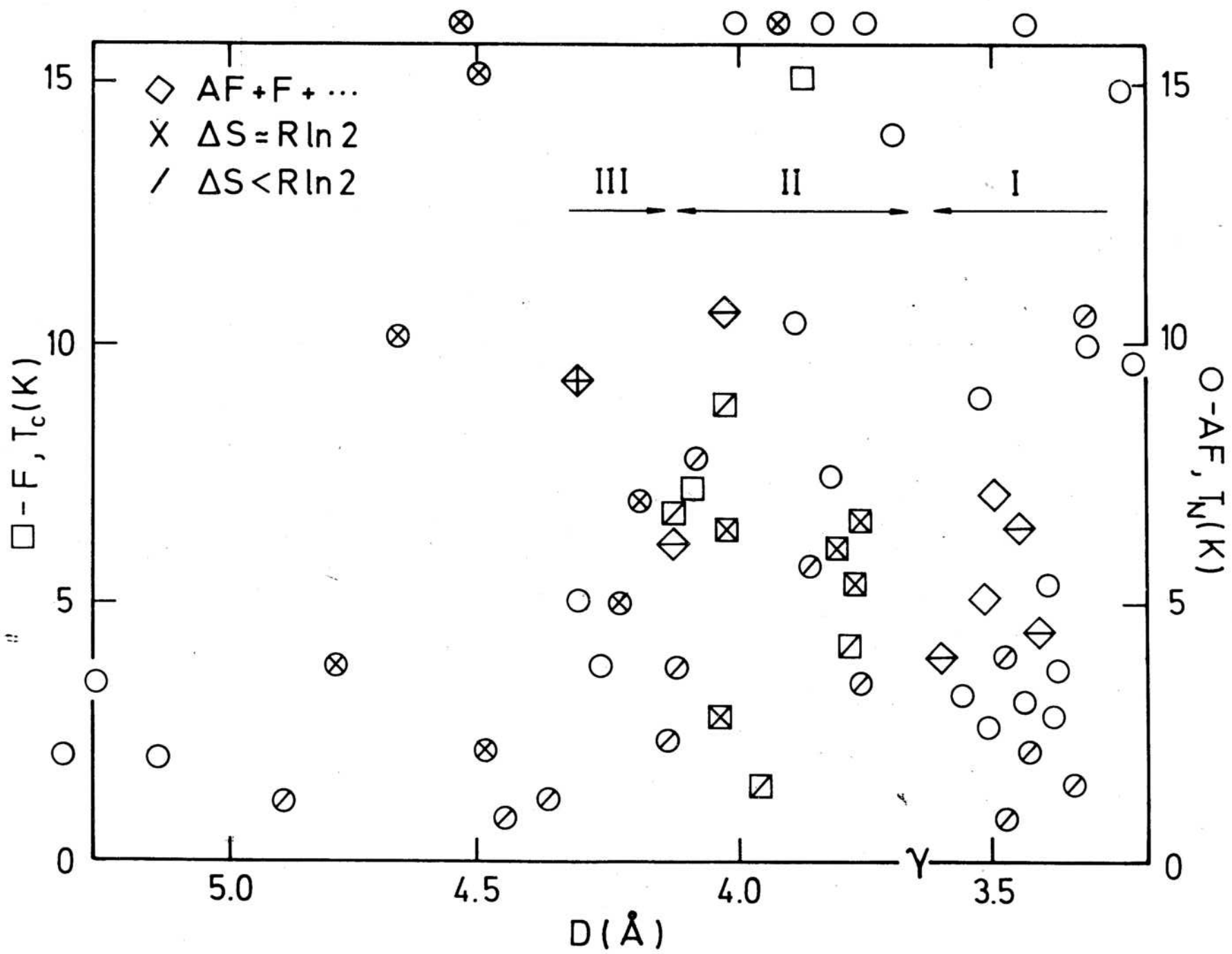
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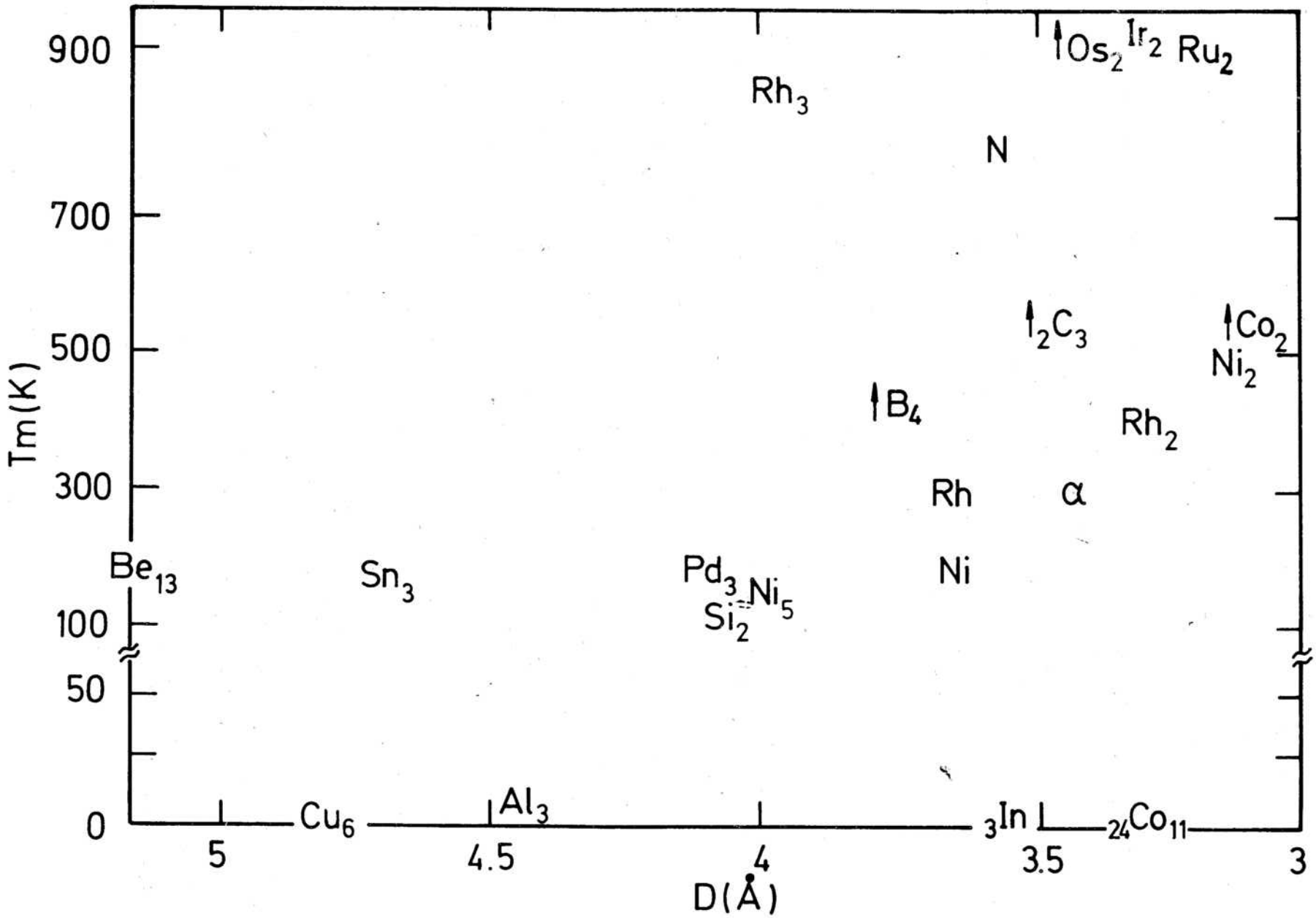
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