Research Article

Cubic crystal-field states of the Yb^{3+} ions studied by specific-heat experiments♠

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Temperature dependence of the specific heat $c_f(T)$ of the trivalent ytterbium ions have been examined for different energy level schemes realized under the action of cubic crystal-field interactions. The position of the quartet Γ_8 state very strongly influences the temperature course of $c_f(T)$. In case of weak spin-dependent interactions, the case very often met in ytterbium compounds, a large specific heat is expected to occur at low temperatures due to the removal of the Kramers degeneracy. The energy level scheme for the Yb^{3+} ion in YbPdSb with the doublet Γ_6 ground state and the quartet state Γ_8 as the highest state has been derived reconciling all-known experimental results.

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I. INTRODUCTION

Due to the strong intra-atomic Coulomb and spin-orbit interactions the n $4f$ electrons form a strongly-correlated electronic system. Thanks strong spin-orbit interactions the orbital and spin momenta of electrons are so strongly coupled that the total angular momentum J becomes the good quantum number. It is generally accepted view for rare-earth ions. Moreover, the spin-orbit coupling in the Yb^{3+} ion is the strongest among the rare-earth ions what makes the 13 f electrons really the strongly-correlated electron system [1].

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It was Kramers in 1930 who realized the first that the charge-formed ground state of a system with an odd number of electrons is the (Kramers-)doublet state. For the reason of the 3^{rd} thermodynamic law this double degeneracy has to be removed before the system reaches the absolute zero-temperature. It only can be removed spontaneously by spin-dependent interactions that produce an internal magnetic field and breaks the time-reversal symmetry. Physically the necessity argument for the removal of the Kramers degeneracy is similar to the Jahn-Teller–effect argument that Nature tends to a singlet ground state. By the electrostatic charge interactions Nature can effectively produce the singlet ground state in case of an even number of the f electrons only. The Yb^{3+} ion having 13 f-electrons is the Kramers f^{13} electronic system with at least the doublet ground state. The ytterbium compounds are of the great current interest as many of them exhibit properties known as the Kondo-effect or heavy-fermion phenomena.

The aim of this paper is to study the influence on the specific heat of the energy-level scheme of the Kramers ytterbium ions (the f^{13} system) for cubic crystal-field interactions in case of weak spin-dependent (S-D) interactions.

II. THEORETICAL OUTLINE

The Yb^{3+} ion has 13 electrons in the incompletely filled f shell. Their orbital and spin momenta are strongly correlated. In the first-order approximation these correlations are well accounted for by Hund's rules that lead to the ground multiplet $^2F_{7/2}$ with L=3, S=1/2 and J=7/2. The ground multiplet is 8-fold degenerated. This degeneracy is partly removed by crystal-field (CEF) and finally by spin-dependent (S-D) interactions. The localized states can be calculated by considering the following Hamiltonian for the Yb^{3+} ion [1–3]:

$$H_R = \sum\sum B_n^m \; O_n^m + ng^2\mu_B^2(-J\langle J\rangle + 1/2\langle J\rangle^2 \quad (1).$$

The first term is the CEF Hamiltonian written for the lowest multiplet $^2F_{7/2}$ with the Lande factor g = 8/7. The second term represents the spin-dependent interactions between the Yb ions written in the mean-field (MF) approximation with n as the MF coefficient.

The crystal-field Hamiltonian for the cubic symmetry takes the form:

$$H_{cub} = B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4) \quad (2).$$

with only 2 unknown parameters B_4 and B_6. The energy level scheme of the Yb^{3+} ion in the cubic crystal field contains two Kramers doublets (d), Γ_6 and Γ_7, and a quartet Γ_8 (q). Properties of the Yb ion and later

the whole compound depend critically on the realized ground state and the sequence of the energy levels. One can easily learn from handy figures of Lea et al. [4] that the ground state and the sequence depend on the mutual strength of CEF parameters B_4 and B_6, i.e. on the parameter x. The usefulness of the parameterization, with W and x, introduced by Lea et al. [4] relies in the fact that it becomes the one-parameter description of the cubic CEF states as W plays the role of the energy scaling parameter.

III. RESULTS AND DISCUSSION

In this paper I will concentrate on the contribution of the localized states to the specific heat $c_f(T)$. This specific heat is associated with possible excitations to the higher localized states. At present standard programs, available on the written request, exist for calculating the specific heat from localized states provided that the level energies are known. In reality it is just opposite, i.e. from the analysis of different properties including the temperature dependence of the specific heat c(T) one tries to infer the level energies. Before going to details it is useful to note that the presence of three CEF levels introduces in the system three energy scales that are associated i) with the splitting of the Kramers doublet ground state (this energy scale is defined by δ_K), ii) with the separation to the first excited CEF level (Δ_K) and iii) to the second excited level (Δ_{CF}, that is here equal to the CEF splitting). These three scales will be called low, mean and high-energy scales, respectively. Appropriate temperature regions, δ_K/k_B, Δ_K/k_B and Δ_{CF}/k_B, k_B is the Boltzmann constant, will be called similarly. The temperature dependencies of the specific heat are shown in Figs 1a-c for different possible combinations of the localized levels, i.e. the quartet-doublet-doublet (q-d-d), doublet-quartet-doublet (d-q-d), and doublet-doublet-quartet (d-d-q) sequence. The CEF parameters have been chosen, with the help of the figure of Lea et al. [4] with J=7/2, in order to produce in all cases the energy level scheme with localized states at 20 K and 400 K. Such the choice allows the clear presentation of the $c_f(T)$ course. Inspecting the figures 1a-c one notices the large influence of the energy level scheme on the temperature dependence of the specific heat. In particular, $c_f(T)$ depends critically on the position of the quartet Γ_8 state.

For the doublet ground state two sequences of CEF levels can be realized. In case of the sequence d-q-d the heat is predominantly released at mean-temperature region, see Fig. 1a. In case of the d-d-q the release of the heat occurs in all temperature regions, see Fig.1b. In case of the quartet Γ_8 ground state and the q-d-d sequence one can see, inspecting

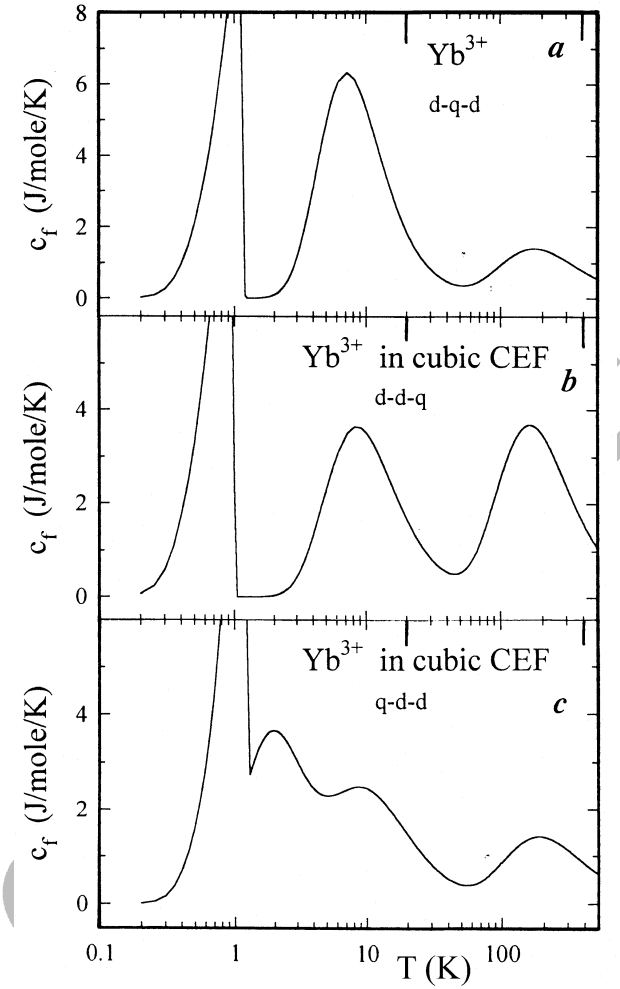

FIG. 1: Temperature dependence of the f contribution to the specific heat of the Yb^{3+} ions in cubic CEF interactions with different energy level schemes with the level sequence d-q-d (a), d-d-q (b) and q-d-d (c). The removal of the Kramers degeneracy of the ground state and the appearance of the magnetic ordering manifests by a large λ-peak at T=1 K. The used CEF parameters are in (a) B_4 = +177 mK and B_6 = -5.48 mK or W = -17.57 K and x = -0.607; in (b) B_4 = +39 mK and B_6 = +9.45 mK or W = 14.26 K and x = 0.165 and in (c) B_4 = -226 mK and B_6 = -4.07 mK or W = -18.7 K and x = 0.726. A peak centered at T = 2 K in (c) is due to the Jahn-Teller splitting on the Γ_8 quartet realized by a tetragonal distortion with B_2^0 = -0.35 K.

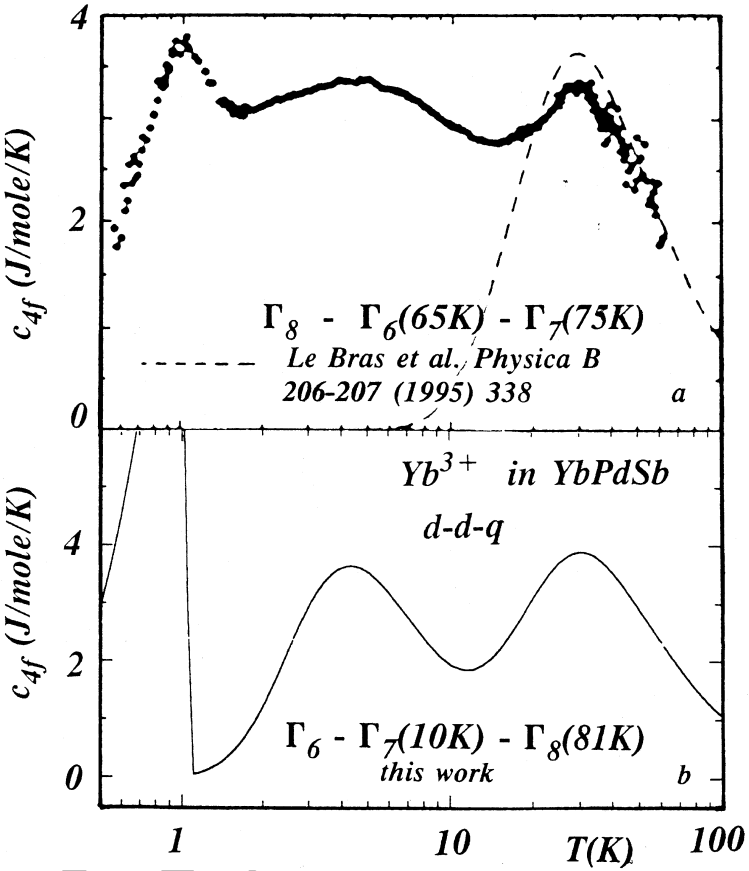

FIG. 2: (a) Measured temperature dependence of the f contribution to the specific heat of the Yb^{3+} ions in the cubic YbPdSb compound, after ref. [8]. The spectrum is similar to that presented in Fig. 1b pointing to the energy level sequence d-d-q. (b) The calculated specific heat of the Yb^{3+} ions with CEF parameters B_4 = +4.35 mK and B_6 = +1.86 mK (W = +2.60 K and x = +0.10) and n = -0.80 T/μ_B; the calculated c_f(T) fully reproduces the maxima positions as well as the absolute value of the specific heat.

Fig. 1c, that the most of the heat is released at low temperatures. This release is associated with the Jahn-Teller effect that splits the quartet into two Kramers doublets. In the present case this Jahn-Teller effect was generated by a small tetragonal distortion, B_2^0 = -0.35 K, yielding a splitting by 5 K. This splitting manifests by an extra maximum of

c_f(T) at 2 K.

For a physical completeness it is worth noting that the ground state of cubic CEF interactions has at least double degeneracy. It results from the Kramers theorem as the Yb^{3+} ion containing the $4f^{13}$ system is the Kramers electronic system. This double Kramers degeneracy can be only removed by spin-dependent interactions, i.e. by an external magnetic field or by an internal molecular field (the second part of the Hamiltonian 1). These spin-dependent interactions, modeled here by the parameter n, have been chosen to be weak, i.e. not to interchange the level positions determined by CEF interactions. S-D interactions remove the Kramers degeneracy what manifests as a χ-type of peak in the c(T) course. In the present calculations a value for n has been adopted in order to form the magnetic state below 1 K.

Consideration of the weak S-D case is physically relevant - there is wide experimental evidence that the magnetic ordering temperature is very small in most of Yb compounds. Many Yb compounds do not show a magnetic ordering down to lowest measured temperatures. This behaviour is understood at present as being due to two effects. At first, the Yb atom, being in the end of the lanthanide series, has the lowest spin, S=1/2. Secondly, the magnetic interactions of the lanthanides decrease strongly with the increasing number of f electrons [5]. In ytterbium monopnictides (N, P, As and Sb), for instance, the Neel temperatures do not exceed 1 K [6, 7].

Inspecting Figs 1a-c one concludes that on basis of the temperature dependence of the specific heat one can infer about the structure of the CEF level scheme provided that the c_f(T) is not masked by other phenomena and that the localized-electron magnetism is giving the essential contribution to the specific heat.

For comparison to experimental data we call for the specific heat of YbPdSb that has been recently measured in ref. 8, Fig.1. These experimental data are recalled in Fig. 2a. Even a quick look at Fig.2a reveals that these experimental data are similar to those presented in Fig. 1b, pointing to the d-d-q sequence of the CEF levels of the Yb^{3+} ion. The experimental data for YbPdSb have three peaks at 1 K, 4 K and 30 K. These peaks are fully reproduced with parameters B_4 = +4.35 mK, B_6 = +1.86 mK (W = +2.60 K and x = +0.10) and n = -0.80 μ_B/T. Although the calculated specific heat is more peaked the agreement between the calculated and the measured dependence c_f(T) is remarkably good. It is worth noting that not only peak-positions but also the absolute values are reproduced. It means, that all ytterbium ions contribute to the specific heat, i.e. all of them are in the trivalent state (within the experimental error). On basis of good reproduction of

the overall dependence $c_f(T)$ one can conclude that the ground state is the doublet. In order to distinguish between Γ_6 and Γ_7 doublets the Mssbauer-spectroscopy result can be used. Namely, the derived value of the magnetic moment of 1.3 μ_B at 0.07 K [9] points to the Γ_6 ground state as $m(\Gamma_6) = 1.33\ \mu_B$. The moment $m(\Gamma_7)$ of 1.71 μ_B is much larger. A discrepancy in description of the specific heat at temperatures close to 1 K must be attributed to imperfections in description of details of the formation of the magnetic state. The broadening of the magnetic transition can be caused by a number of reasons. A site-variation of the Kramers-doublet splitting δ_K, understood in case of a long-wave commensurate/incommensurate magnetic structure, or the Kondo effect that apparently must play a role below 3 K can be mentioned here. The good **overall description** of the temperature dependence of the specific heat provides strong confidence on the Γ_6 **Kramers doublet ground state in YbPdSb**. It is in contrary to the conclusion drawn in ref.8 in favour for the quartet ground state Γ_8 with Γ_6 and Γ_7 above at 65 K and 75 K. The Γ_8-Γ_6-Γ_7 sequence is not at all able to explain the low-temperature part of the $c_f(T)$ below 20 K. It was already admitted by the authors of ref. 8 and is clearly seen in Fig. 2a. In this figure the original theoretical results, shown by the broken line, accounts only for the peak centered at 30 K leaving out of explanation the enormous heat below 20 K. Moreover, the Γ_8-Γ_6-Γ_7 sequence disagrees the magnetic result. The magnetic moment for the Γ_8 state amounts to 2.0 μ_B. It largely exceeds the experimental value of 1.3 μ_B. Thus the present assignment of Γ_6-Γ_7(10K)-Γ_8(81K) is superior to the one with the Γ_8 ground state as it reconciles the above-mentioned experimental results. The doublet Γ_6 has been chosen as the ground state on basis of the Mssbauer-effect result whereas the position of the second doublet Γ_7 and the quartet Γ_8 is defined by the specific-heat result. The relatively weak size of CEF interactions in YbPdSb of 81 K (7.5 meV) is supported by inelastic-neutron-scattering (INS) experiments on isostructural and isoelectronic compound YbPtBi (written usually as YbBiPt). INS experiments on YbBiPt reported in ref. 10 have revealed the overall CEF splitting of 5.7 meV (66 K). It indicates that CEF interactions in these compounds are of similar size what is a desired fact from the point of view for looking for the consistent picture of CEF interactions in cubic isostructural and isoelectronic compounds. From this point of view it is worth noting YbSb that has also the cubic structure with similar lattice parameters, of 6.06 and 6.45 $\mathring{A}$ [9] for YbSb and YbPdSb respectively. The Γ_6 ground state, i.e. the same as presently inferred for YbPdSb, has been deduced in ref. 6 for YbSb. For the full scientific honesty it is necessary to add that the localized crystal-field excitations in YbSbPd (of

course, it is the same as YbPdSb) has been observed by Marshall [12], as mentioned in ref.10. The present author does not know about his level assignment as ref. 12 is Ph.D. thesis of London University. The present author has undertaken some efforts to get a copy of this Thesis. Surely, it will of the large scientific interest to compare the electronic structure obtained by different experimental techniques. The most important is, however, the fact there is steadily growing evidence for the existence of localized crystal-field states in these exotic ytterbium compounds.

IV. CONCLUSIONS

The large influence on the temperature dependence of the specific heat of the energy-level scheme of the Kramers ytterbium ions have been analyzed for cubic crystal-field interactions. The position of the quartet Γ_8 state very strongly influences the temperature course of c_f(T). In case of weak spin-dependent interactions there occurs large specific heat at low temperatures associated with the removal of the Kramers degeneracy. In general, weak S-D interactions do not interchange the level sequence determined by crystal-field interactions [1]. The energy level scheme for the Yb^{3+} ion in YbPdSb with the doublet Γ_6 ground state and the quartet state Γ_8 as the highest state has been derived reconciling all-known experimental results. The 3-peak structure of the c_f(T) in YbPdSb results from the three different energy scales determined by the splitting of the Kramers-doublet ground state δ_K of 1 K, by the separation to the first excited CEF level Δ_K of 10 K and of the overall crystal-field splitting Δ_{CF} of 81 K. The experimental value of the low-temperature magnetic moment of 1.3 μ_B is exactly explained. The good quantitative reproduction of the specific-heat data, i.e. the temperature positions and the absolute values, is of great importance as it indicates that almost all, if not all, Yb ions are in the trivalent state in YbPdSb. It is a hope that the present studies will help to understand properties of ytterbium compounds. Even those exhibiting the heavy-fermion or Kondo-effect behaviour. Surely, for the evaluation of these exotic effects conventional crystal-field and spin-dependent phenomena have to be correctly calculated. It is of extreme importance to the heavy-fermion problem to note that the extremely large specific heat found at low temperatures, even below 1 K, does not mean that the f states lie at the Fermi level [13]. It has been already pointed out a few years ago that the f excitations can be very small in energy, giving a substantial contribution to the low-temperature specific heat, despite of the fact that f states are lying a few eV below the Fermi level [14]. This is obvious if one realizes that f excitations are many-electron excitations whereas the Fermi

level is associated with single-electron excitations. These ideas are behind a theory presented from 1992 [14] by the present author for the understanding the heavy-fermion phenomena with the localized f electrons. According to this theory the heavy-fermion phenomena are associated with difficulties in the removal of the Kramers degeneracy of the localized ground state. One of very important prediction of this theory was that heavy-fermion-like phenomena [14–16] can occur in an insulating compound as is the case of YbPdSb [9]. The presented interpretation of the specific heat is in general agreement with authors of refs 6,7,9,10,12 that much of physics of exotic ytterbium compounds is associated with the localized low-energy crystal-field excitations.

♠ This paper is slightly modified version of the paper of 10.03.1997 that has been rejected by the referee with an argument that I did not refer to W. G. Marshall Ph.D. thesis. It does not change the main message of this paper that much of physics of exotic ytterbium compounds is associated with the localized low-energy crystal-field excitations.

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