MAGNETIC PROPERTIES OF ANTIFERROMAGNETICALLY ORDERED KRAMERS LIGHT RARE-EARTH COMPOUNDS. PART I

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The magnetic behaviour of antiferromagnetic Kramers light rare-earth compounds is examined within the framework of the molecular-field approximation including an external magnetic field. Numerical calculations are performed for cerium compounds, having the simple rock-salt structure. The influence of tetragonal distortion is studied too. Part I of the present paper comprises a detailed analysis of the crystal-field-only effects which determine essentially the magnetic properties of such systems.

1. *Introduction*

As known, crystal-field effects play a hey role in light rare-earth compounds in determining their magnetic properties and collective excitations, especially if the energy gaps between the lower-lying crystal-field energy levels are of the same order as the exchange coupling.

The main purpose of our paper is to study the magnetic properties of light rare-earth compounds exhibiting Kramers degeneracy of their crystal-field energy levels. The majority of these compounds orders antiferromagnetically (see for example [1–11]). We focus our attention on the antiferromagnetic cerium compounds having the simple rock-salt structure which are well-snited for theoretical investigation (see [2–5]). We shall be studying their magnetic properties applying a simplified model which preserves, however, the main features of the actual systems. In the ordered phase, the Ce^{+3} ions form two interpenetrating sublattices. We assume, moreover, that the nearest neighbours of an ion of one sublattice belong only to the other sublattice (cf. [10, 11]). As it is well known, antiferromagnetic systems have many features not exhibited by ferromagnets, especially in the presence of an external magnetic field. In this paper, we have recourse to the molecular-field approximation including an external magnetic field applied along the magnetic-order axis (see [1–3, 10, 11]). Since if it is well established that the magnetic behaviour of light rare-earth compounds is mainly determined by their crystal-field

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properties, the first part of the present paper is devoted to a closer analysis of the latter. In Part II, we shall consider the antiferromagnetic and paramagnetic regions and discuss the question of how exchange coupling influences the crystal-field-only effects.

2. *The crystal field*

The crystal-field Hamiltonian for a Ce^{+3} ion in cubic environment with tetragonal distortion can be written as follows (see e.g. [2]):

$$\hat{H}_{cf} = B_4(O_4^0+5O_4^4)+B_2O_2^0, \tag{1}$$

where O_l^m are the well-known Stevens operators. As clearly seen, all the crystal-field-only quantities can be expressed in terms of but two parameters: B_4 and $\delta = B_2/B_4$. The latter arises due to the tetragonal distortion and quantitatively determines its contribution, compared to the "pure" cubic case ($\delta = 0$). In cubic environment, the crystal-field operator gives rise to a splitting of the ground-state multiplet of the free Ce^{+3} ion into a Γ_7-doublet and Γ_8-quartet. The energy gap between the doublet and quartet amounts to $\Delta_{cf} = 360\,B_4$. Due to the tetragonal distortion, the quartet is also split into two doublets and the energy gap between them is determined by the magnitude of δ.

The sign of B_4 determines the crystal-field ground-state: for $B_4 > 0$, this is a Γ_7-doublet. In the present paper, we discuss only this case since it gives rise to a number of anomalies in the magnetic behaviour of the system mainly due to a crossing of the lower-lying magnetic singlets (cf. also [2, 5, 13]).

We perturb the crystal-field Hamiltonian by the appropriate Zeeman term and, thus, the total single-ion hamiltonian is

$$\hat{H} = \hat{H}_{cf}-H_z\hat{J}^z, \tag{2}$$

where $\hat{J}^z$ is the operator of the z-component of total angular momentum. The external magnetic field strength H_z is expressed in units of energy. The z-axis is directed along one of the cubic four-fold axes e.g. the (001) direction.

After very simple algebra, diagonalization of the Hamiltonian $\hat{H}$ in the basis of the crystal-field eigen-states provides six energy levels and the appropriate six eigen-states (see e.g. [2, 3, 5, 13]). Once these are available, we can obtain the temperature averages of all the crystal-field-only quantities of interest from the magnetic point of view such as: magnetization, susceptibility, and specific heat.

The crystal-field parameter B_4 takes the following values: $B_4 = 0.02778$ K, $B_4 = 0.05556$ K, $B_4 = 0.08333$ K, $B_4 = 0.16667$ K. The results presented in Part I will be compared with those calculated including the crystal-field and exchange effects in Part II. The Néel temperature T_N is fixed and equal to 20 K. Therefore by varying B_4 we also vary the ratio of the crystal and exchange fields through the range of our interest (cf. also [2, 3]). The tetragonal contribution parameter has to be negative from cubic single-ion anisotropy considerations (see e.g. [12]). For our further analysis, we take δ from the range -5. For values within this range, δ does not influence appreciably the crystal-field-only quantities. In the diagrams we show, as an example, the curves for $\delta = -5$.

Cooper suggested (see [3]) that, in cerium monopnictides, the crystal-field-effects plus anisotropic exchange interaction can explain all the anomalies in the behaviour of the magnetic quantities. In our model considerations we have chosen, however, the usual bilinear form of exchange coupling and have obtained that the majority of anomalies can be interpreted in terms of the crystal field combined with the exchange, only.

3. *Crystal-field-only magnetization*

The magnetization per Ce^{+3} ion (in units of $g\mu_B$) can be derived from the following formula:

$$M_0(H_z, T) = Z^{-1} \sum_{i=1}^{6} \langle \Gamma_i, J^z \Gamma_i \rangle e^{-E_{\Gamma i}/\theta}, \tag{3}$$

where Z is the partition function, and

$$Z = \sum_{i=1}^{6} e^{-E_{\Gamma i}/\theta}, \quad \theta = kT. \tag{3a}$$

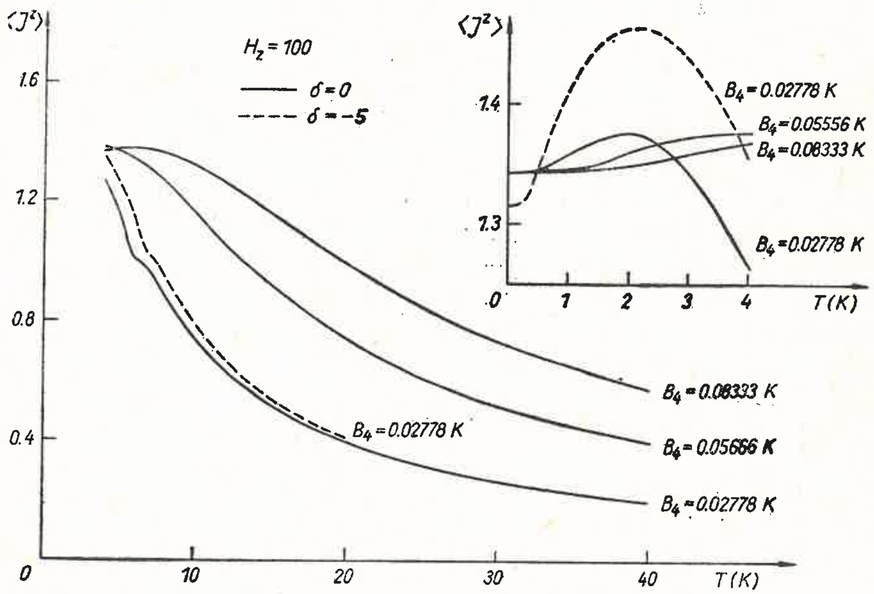


Fig. 1. The temperature-dependence of the crystal-field-only magnetization in the external field $\tilde{H}_z$. Magnetization is expressed in units of $g\mu_B$ (g — Laudé's factor, μ_B — Bohr magneton). The magnetic field strength is given in the dimensionless form: $g\mu_B H_z/B_4 = \tilde{H}_z$. The additional diagram at the top right-hand corner shows the temperature dependence of $\langle J^z \rangle$ for the low-temperature range

Obviously, E_{Γ_i} and $|\Gamma_i\rangle$ are the eigen-values and eigen-states of the Hamiltonian $\hat{H}$, respectively. The function $M_0(H_z, T)$ is studied both with respect to its temperature--dependence and with respect to its dependence upon the external magnetic field. The results are shown in Figs 1, 2. The temperature-dependence of the crystal-field-only magnet-

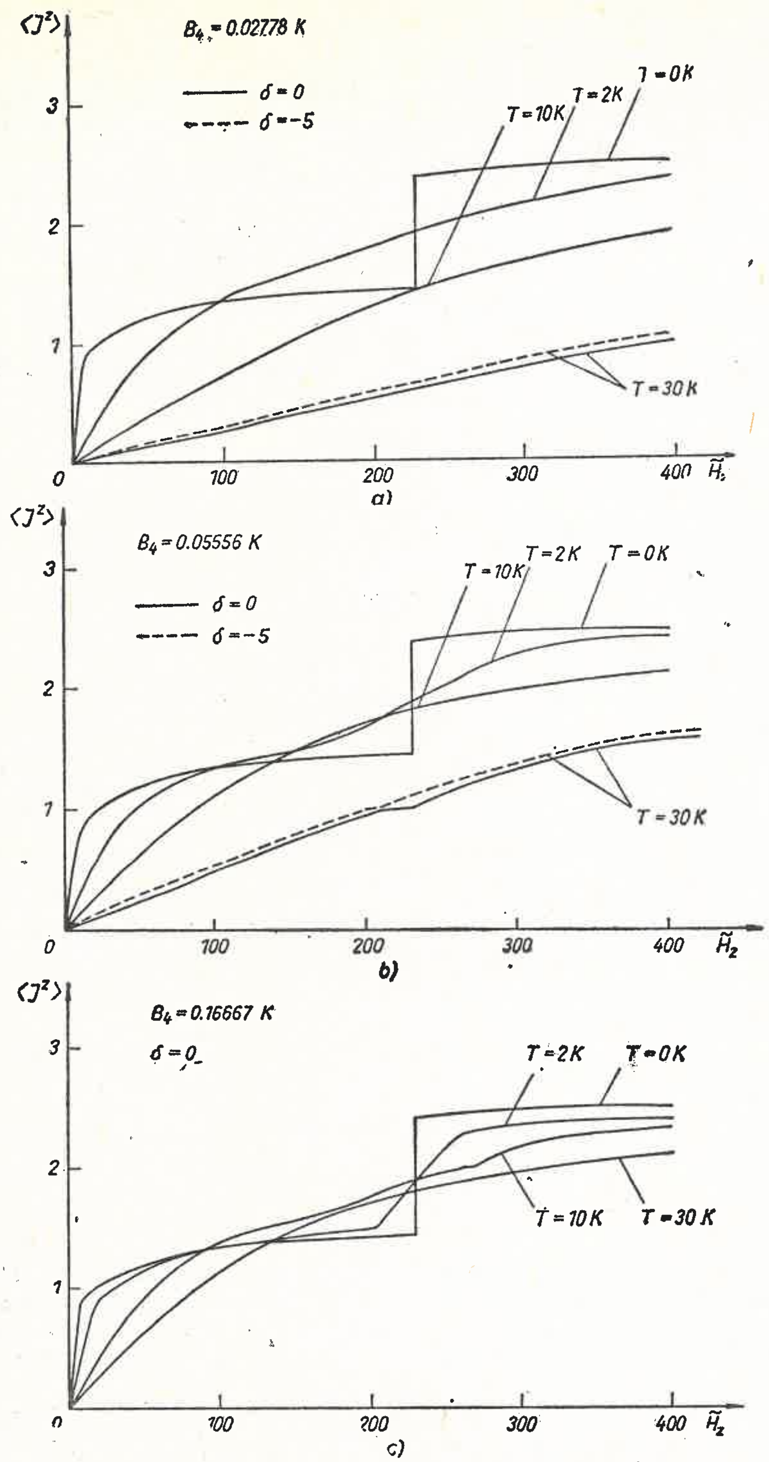


Fig. 2. The crystal-field-only magnetization against the magnetic field strength $\tilde{H}_z$ at different temperatures. Magnetization is expressed in units of $g\mu_B$; the magnetic field strength is given as $\tilde{H}_z = g\mu_B H_z/B_4$, a) $B_4 = 0.02778$ K, b) $B_4 = 0.05556$ K, c) $B_4 = 0.16667$ K

ization is very sensitive both to the crystal-field parameters B_4 and δ and to the strength of the applied field.

The temperature-dependence of the crystal-field-only magnetization is very sensitive to the magnitude of the energy gap between the crystal-field ground-state doublet and the excited quartet. With increasing temperature, the magnetization decreases rather slowly. Anomalies in temperature-behaviour occur in the low-temperature region and for smaller values of B_4 (see the additional diagram in Fig. 1) and are due to an increase in thermal population of the second magnetic singlet, originating in the Γ_7-doublet under the action of the external field. As seen, the influence of the tetragonal distortion is stronger at lower temperature and gives rise to a quantitative change in the temperature-dependence of $\langle J^z \rangle$. In Figs 2 a, b, c we have plotted the crystal-field-only magnetization versus the applied field strength at four different temperatures. As seen, the anomalies occur at lower temperatures and, rather, for larger values of B_4. The behaviour of the $\langle J^z \rangle$-function is of particular interest at $T = 0$ K; the magnetization is then equal to the quantum-average of the operator $\hat{J}^z$ over the ground-state of the Ce^{+3} ion. With increasing field, the magnetization first sharply grows, and then remains essentially unchanged for a long region of the field. At the upper end of this region, for which the magnetic singlets originating in the Γ_7-doublet intersect, there is the sharp jump after which the magnetization again slightly varies with increasing field. A similar behaviour of $\langle J^z \rangle$ occurs also for $B_4 = 0.16667$ K at $T = 2$ K, although the jump in magnetization accompanying the crossing of the lower-lying energy levels is not so sharp as that at $T = 0$ K. At higher temperatures and for smaller values of B_4, when the thermal populations of all the six energy levels play an essential role, the $\langle J^z \rangle$--curves become smooth and tend to the Brillouin function of $J = 5/2$ (see for example [1, 5]). The curves for $\delta = -5$ do not depart essentially from the appropriate $\delta = 0$-curves.

4. *The crystal-field-only susceptibility*

The parallel susceptibility in units of $g^2\mu_B^2$ is given by the following formula (see for example [1, 2, 5, 10, 11]):

$$\chi_{cf}(T, H_z) = \frac{\partial \langle J^z \rangle}{\partial H_z}. \tag{4}$$

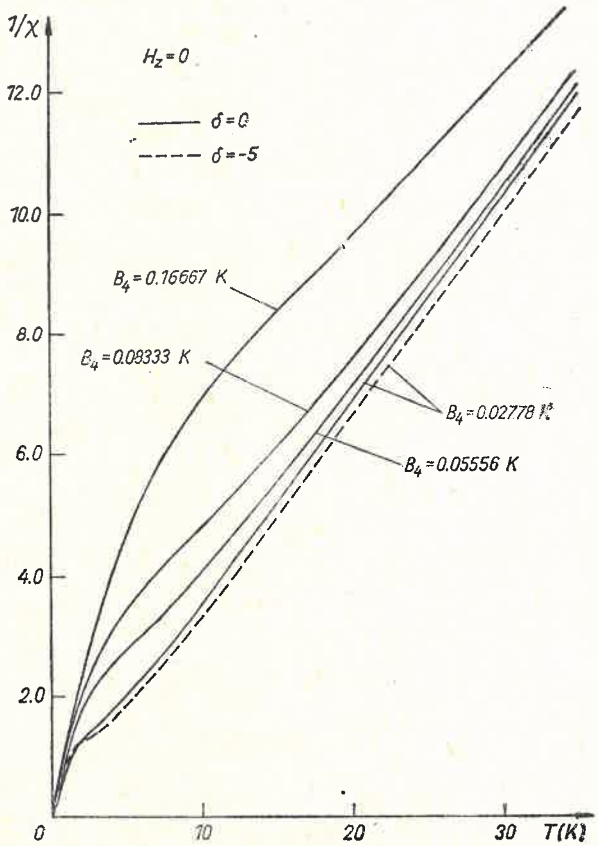
On writing the derivative in explicit form, one obtains

$$\chi_{cf}(T, H_z) = \frac{1}{\theta} \cdot \frac{1}{Z} \sum_{\substack{i,j=1 \\ (E_{\Gamma_i}=E_{\Gamma_j})}}^{6} \langle \Gamma_i, J^z \Gamma_j \rangle^2 e^{-E_{\Gamma_i}/\theta}$$

$$-\frac{1}{\theta}\left\{\frac{1}{Z} \sum_{\substack{i,j=1 \\ (E_{\Gamma_i}=E_{\Gamma_j})}}^{6} \langle \Gamma_i, J^z \Gamma_j \rangle e^{-E_{\Gamma_i}/\theta}\right\}^2 + \frac{2}{Z} \sum_{\substack{i,j=1 \\ (E_{\Gamma_i}\neq E_{\Gamma_j})}}^{6} \frac{|\langle \Gamma_i, J^z \Gamma_j \rangle|^2}{E_{\Gamma_i} - E_{\Gamma_j}} e^{-E_{\Gamma_i}/\theta}. \tag{4a}$$

For $H^z = 0$, the eigen-values and eigen-functions of the total Hamiltonian $\hat{H}$ go over into the appropriate eigen-values and eigen-functions of the crystal-field Hamiltonian $\hat{H}_{cf}$ (see: [1, 2]). The first two terms fo Eq. (4a) give the so-called Curie–Langevin contribution, whereas the third term is the Van Vleck-type contribution to the static susceptibility. Both the temperature behaviour and external field-dependence of the susceptibility can be clearly interpreted if one keeps in mind the simultaneous occurrence of these two contributions. The first is strongly temperature-dependent by way of the factor $1/\theta$ and indirectly through the thermal populations of the energy levels; the Van Vleck-type term is temperature-dependent only by way of the thermal populations of the energy levels.

In the case of systems exhibiting Kramers degeneracy of their crystal-field energy levels, both contributions to the susceptibility exist always. The temperature-dependence of the inverse susceptibility is plotted in Figs 3 a, b, c. As seen, the curves are very sensitive both to the crystal-field parameter B_4 and the magnitude of the external magnetic field H^z. At higher temperatures, the susceptibility behaviour is determined by the Curie contribution whereas with decreasing temperature the curve deviates significantly from the



a)

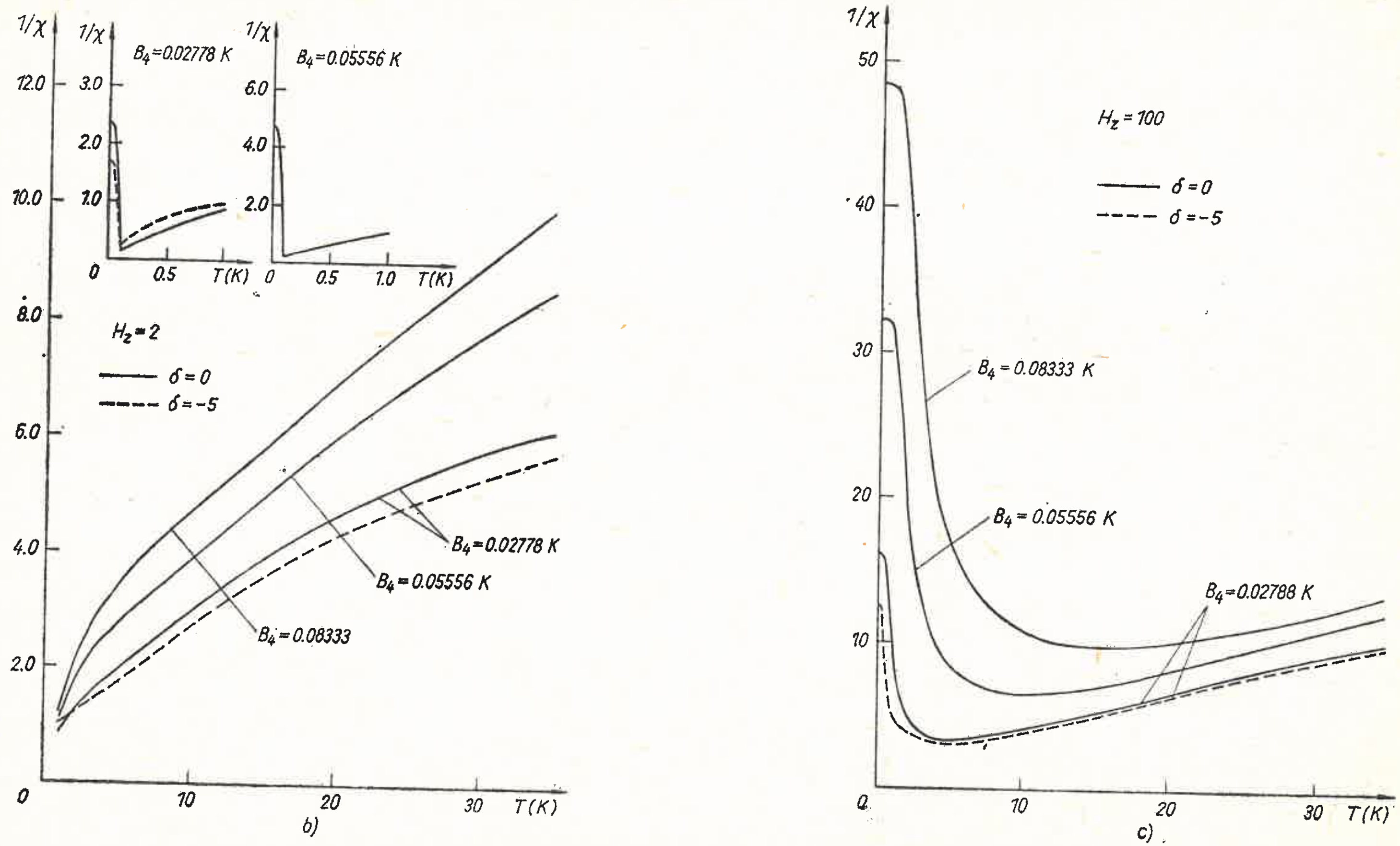
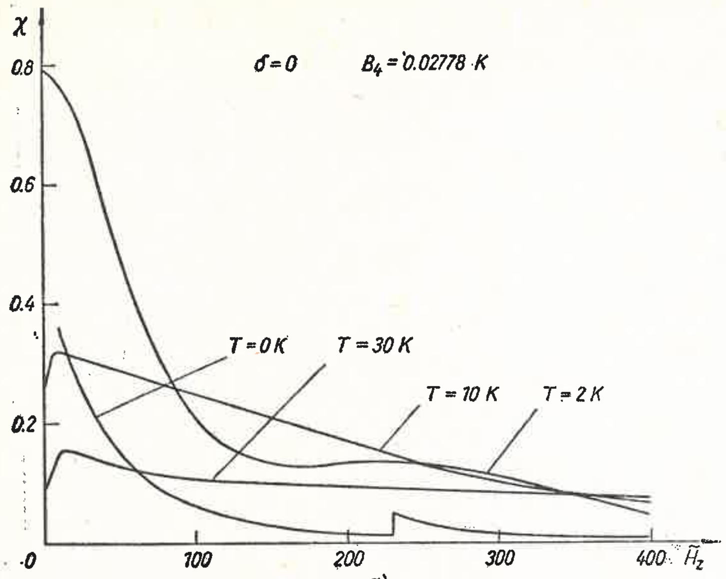
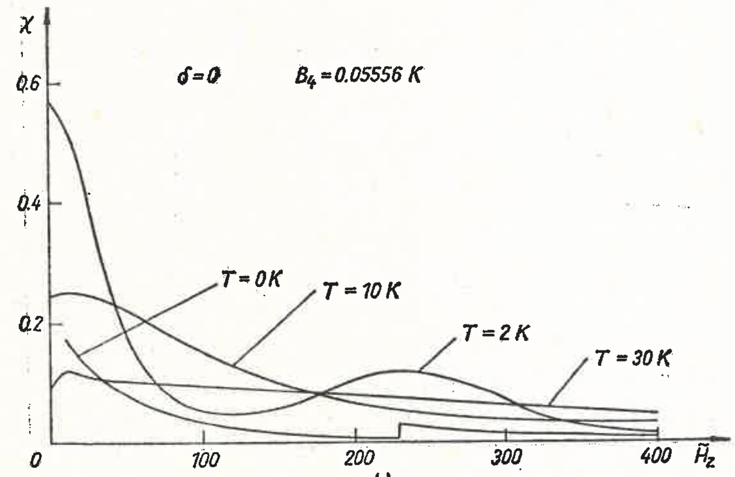


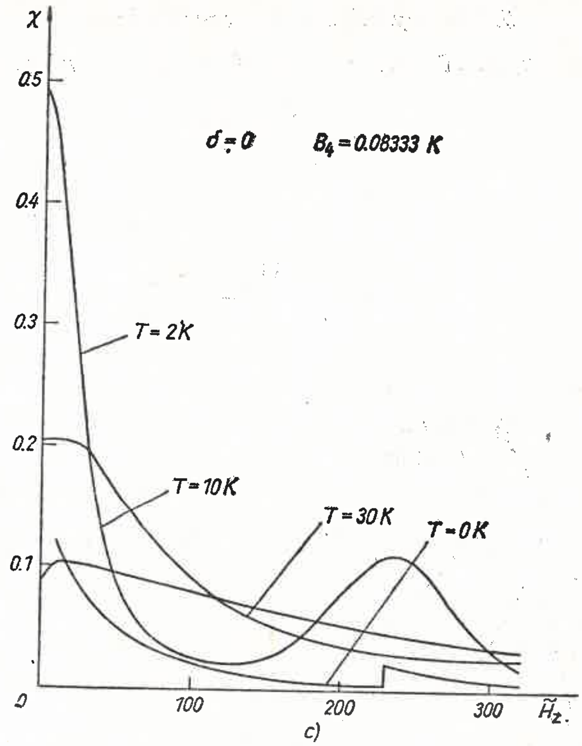
Fig. 3. The temperature-dependence of the crystal-field-only inverse susceptibility. Susceptibility is expressed in units of $g^2\mu_B^2$. a) $\tilde{H}_z = 0$, b) $\tilde{H}_z = 2$. The additional diagrams show the low-temperature region, c) $\tilde{H}_z = 100$


χ
0.8
0.6
0.4
0.2
0
$\delta = 0$
$B_4 = 0.02778$ K
T = 0 K
T = 30 K
T = 10 K
T = 2 K
100
200
300
400
$\tilde{H}_z$

a)


χ
0.6
0.4
0.2
0
$\delta = 0$
$B_4 = 0.05556$ K
T = 0 K
T = 10 K
T = 2 K
T = 30 K
100
200
300
400
$\tilde{H}_z$

b)



c)

Fig. 4. The crystal-field-only susceptibility against the magnetic field strength $\tilde{H}_z$ at different temperatures. Susceptibility is expressed in units of $g^2\mu_B^2$. The magnetic-field strength is given by $\tilde{H}_z = g\mu_B H_z/B_4$. a) $B_4 = 0.02778$ K, b) $B_4 = 0.05556$ K, c) $B_4 = 0.08333$ K

nearly straight line due to the Van Vleck-type contribution. Figs 4 a, b, c show the dependence of the susceptibility on the external field at four different temperatures. For all three values of B_4, the respective curves do not diverge significantly from one another, At $T = 0$ K, we make use of the following formula for the susceptibility:

$$\chi_{cf}(0, H_z) = \frac{\partial E_0}{\partial H_z}, \tag{4b}$$

where E_0 is the ground energy-level of the Hamiltonian $\hat{H}$. With no external field, however, the susceptibility χ_{cf} tends to infinity with $T \to 0$. At $T = 0$ K there occurs a characteristic jump which corresponds to a change in the ground-state due to the crossing of the lower--lying magnetic singlets. For the same value of the external field, there appears a different peak at $T = 2$ K because the thermal populations of both lower-lying magnetic singlets become comparable and even equal to each other. At higher temperatures e.g. $T = 10$ K and 30 K the behaviour of the susceptibility is predominantly determined by the Curie–Langevin term and the anomalies appear only for small values of the external field.

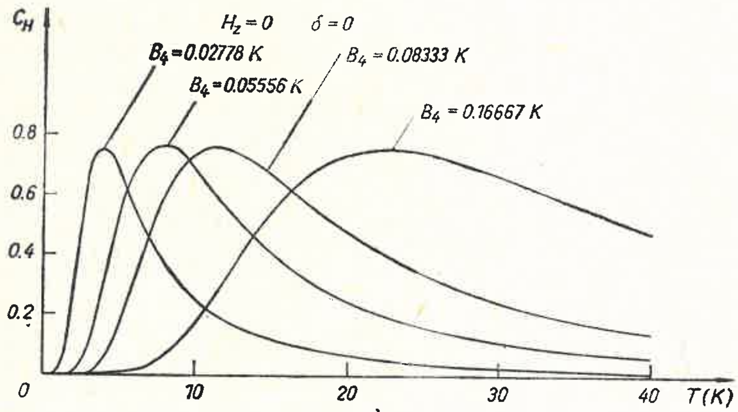
5. *The crystal-field-only specific heat*

The crystal-field-only specific heat is derived from the following formula (see also [10])

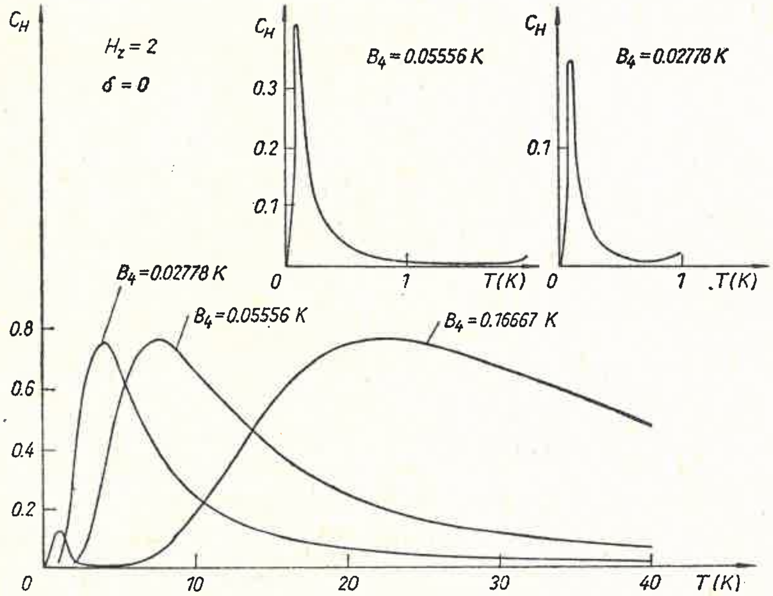
$$C_H = \left(\frac{\partial\langle\hat{H}\rangle}{\partial\theta}\right)_H, \tag{5}$$

where

$$\langle\hat{H}\rangle = \frac{1}{Z}\sum_{i=1}^{6} E_{\Gamma_i} e^{-E_{\Gamma_i}/\theta}. \tag{5a}$$



a)



b)

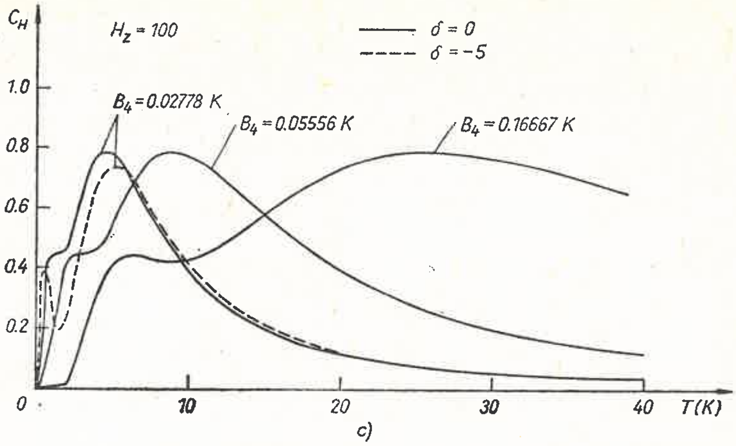


Fig. 5. The crystal-field-only specific heat C_H against the temperature at the different applied field strengths $\tilde{H}_z$: a) $\tilde{H}_z = 0$, b) $\tilde{H}_z = 2$. The additional diagrams show the low-temperature region, c) $\tilde{H}_z = 100$

In Figs 5 a, b, c we have plotted the specific heat against the temperature at three different values of the external field.

With no external field, the curves are strongly dependent on the crystal-field parameter B_4. The different peaks are related with the Schottky anomaly, corresponding to the energy gap between the crystal-field ground doublet and the excited quartet. In the presence of an external field, there appears an additional peak at very low temperatures (see Figs 5b and 5c). The occurrence of these peaks can be attributed to the splitting of the lower-lying doublet due to the external field. The energy gap between the magnetic singlets gives rise to another Schottky anomaly. The position of these additional peaks is determined both by the strength of the external field and by the crystal-field parameters B_4 and δ. The final conclusions will be drawn on comparison of the preceding results with those concerning exchange coupling of the Ce^{+3} ions in Part II of this paper.

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