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# Magnetic susceptibility of the Van Vleck paramagnet $\text{Cs}_5\text{Eu}(\text{N}_3)_8$

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**Abstract.** The magnetic susceptibility of the new compound  $\text{Cs}_5\text{Eu}(\text{N}_3)_8$  has been measured in the temperature range from 77 to 300 K. From excitation and luminescence spectra the compound is known to contain two distinct but very similar  $\text{Eu}^{3+}$  sites with approximately  $D_{4d}$  microsymmetry. The experimental susceptibility data are interpreted in terms of the Van Vleck theory for closely spaced multiplets. A perfect fit to this model is obtained on the assumption that the two sites with energies as observed in the emission spectra are present in equal proportions.

## 1. Introduction

Among the rare-earth ions,  $\text{Eu}^{3+}$  occupies a unique position in that there are energy levels fairly close to the singlet ground state  ${}^7F_0$ . The excited states  ${}^7F_1$  and  ${}^7F_2$  are only about 370 and 1000 wavenumbers to higher energy in the free ion. There is no ground-state magnetic susceptibility in  $\text{Eu}^{3+}$  ( $J = 0$ ), but the splitting of the excited states by a surrounding crystal field and the thermal population of the crystal-field levels cause a second-order contribution to the magnetic susceptibility. This behaviour was first predicted by Van Vleck [1].

There have been several successful attempts in the literature to correlate experimental data with Van Vleck's theory [2-4]. All these investigations were carried out on highly ionic compounds with ligands such as  $\text{F}^-$  and  $\text{O}^{2-}$  with only one possible microsymmetry for the  $\text{Eu}^{3+}$  ion in the lattice. It was not clear whether this approach would lead to acceptable results in the case of  $\text{Cs}_5\text{Eu}(\text{N}_3)_8$  with the dumb-bell-shaped azide ions  $\text{N}_3^-$  as ligands and with two distinct sites for  $\text{Eu}^{3+}$ . For the quantitative calculation of the susceptibility the energies of the crystal-field split first excited state  ${}^7F_1$  and the barycentre for the second excited state  ${}^7F_2$  determined from luminescence data were used.

## 2. Experimental details

The preparation of single crystals of  $\text{Cs}_5\text{Eu}(\text{N}_3)_8$  has been described elsewhere [5]. The material forms pale-yellow-coloured crystals and is sensitive to moisture and ambient atmosphere. Therefore, careful handling is necessary. The crystals were stored in a dry nitrogen atmosphere until required for measurements. All manipulations including grinding of the crystals were carried out under a flush of dry nitrogen gas.

Bulk magnetic susceptibility measurements were performed on freshly ground material with the modified Faraday balance SUS 10 (manufactured by A Paar KG, Graz, Austria) between 77 and 300 K using a magnetic flux density of 1.3 T. A typical mass per run was 20 mg of azide. The equipment was calibrated with  $\text{Hg}[\text{Co}(\text{NCS})_4]$  according to Bünzli [6].

The experimental details of the spectroscopic investigation have been given elsewhere [7].

### 3. Structural and spectroscopic information

The crystal structure of the new material was determined at room temperature with x-ray single crystal methods [5]. It was found that each  $\text{Eu}^{3+}$  ion is surrounded by eight azide groups, and that individual  $[\text{Eu}(\text{N}_3)_8]^{5-}$  polyhedra are well separated from each other. The mean Eu–Eu distance is about 9 Å. Neighbouring polyhedra do not share  $\text{N}_3^-$  groups. Therefore, magnetic exchange via azide bridges is not to be expected. Considering only nearest-neighbour N atoms, the polyhedra show a distorted  $D_{4d}$  tetragonal symmetry around the central  $\text{Eu}^{3+}$  ions. From the x-ray data there is no indication for the existence of different sites within the material. On the other hand, there is clear evidence for two major sites (I and II) from high resolution excitation spectroscopy in the  ${}^7F_0 \rightarrow {}^5D_0$  region [7]. It was possible to determine the crystal-field energies of the first excited state  ${}^7F_1$  from the  ${}^5D_0 \rightarrow {}^7F_1$  luminescence for both sites. The energy level diagram is given in figure 1.

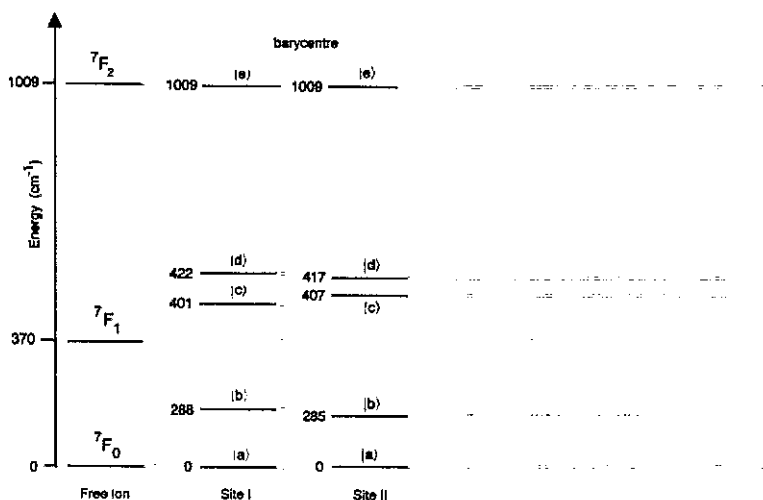


Figure 1. Energy level diagram (not to scale) indicating the states and energies of  $\text{Eu}^{3+}$  in the two sites of  $\text{Cs}_5\text{Eu}(\text{N}_3)_8$  used in this work. All numbers are wavenumbers relative to the unsplit ground state.

The discrepancy in the number of sites found by x-ray and by spectroscopic methods may arise from the different temperatures at which data were collected (300 K for x-ray data, and 77 K and 4 K for luminescence and excitation spectra, respectively) and/or from the nature of the two experimental methods [8, 9]. X-ray data yield averaged representations of the coordination polyhedra, whereas spectroscopic

measurements may reflect individual conformations, thus producing several different spectra for what is found to be a single crystallographic site by x-ray methods. There are no indications for a phase transition within the whole temperature range. A possible explanation for the different nature of sites I and II has been given in the spectroscopic paper [7].

#### 4. Calculations

When dealing with magnetic susceptibilities in crystals the master equation is the well known Van Vleck equation

$$\chi_M^{(i)} = D \sum_n \left( \frac{\alpha_n^2}{kT} + \sum_{m \neq n} \frac{2\alpha_{nm}^2}{E_m - E_n} \right) \exp\left(-\frac{E_n}{kT}\right) \quad (1)$$

where the superscript  $i$  signifies the principal axis ( $i = x, y, z$ ) and the indices  $n$  and  $m$  denote the relevant states;  $E_n$  and  $E_m$  are the corresponding energies. When equation (1) is used to fit experimental bulk susceptibility data of powdered samples with randomly oriented microcrystals, one has to use the average

$$\chi_M = \frac{1}{3} (\chi_M^{(x)} + \chi_M^{(y)} + \chi_M^{(z)}). \quad (2)$$

The factor  $D$  in equation (1) is defined by

$$D = N_A \mu_0 \mu_B \left[ \sum_n \exp\left(-\frac{E_n}{kT}\right) \right]^{-1} \quad (3)$$

with the Avogadro constant  $N_A$  and the Bohr magneton  $\mu_B$ .  $\alpha_n$  and  $\alpha_{nm}$  in equation (1) are the first- and second-order Zeeman matrix elements defined as

$$\alpha_n = \langle n | L + 2S | n \rangle$$

and

$$\alpha_{nm} = \langle n | L + 2S | m \rangle.$$

It is well known that the  $\alpha_n$ -terms are responsible for the Curie behaviour of paramagnets, whereas the  $\alpha_{nm}$ -terms give rise to the so-called temperature-independent contribution to the magnetic susceptibility.

For rare-earth ions the effect of the surrounding crystal-field is a minor perturbation to the free-ion system. Using first-order perturbation theory, the system may be described by its free-ion wavefunctions and the crystal-field energies obtained from the spectroscopic experiments. A convenient basis set including the unsplit ground state  ${}^7F_0$  and the crystal-field split excited state  ${}^7F_1$  in  $|J, M\rangle$  notation is

$$\begin{aligned} |a\rangle &= |0, 0\rangle \\ |b\rangle &= |1, 0\rangle \\ |c\rangle &= (1/\sqrt{2})(|1, 1\rangle + |1, -1\rangle) \\ |d\rangle &= (1/\sqrt{2})(|1, 1\rangle - |1, -1\rangle) \end{aligned} \quad (4)$$

where the short-hand notation on the left-hand side is chosen according to the nomenclature in figure 1. It turns out that the magnetic susceptibility becomes rapidly insensitive to the detailed energy level structure of the higher excited states. Therefore, below 300 K, it is quite feasible for the theoretical treatment to approximate the  ${}^2F_2$  multiplet by its barycentre ( $|e\rangle$  in figure 1) only. In the case under investigation, all crystal-field states are singlets and therefore there is no first-order Zeeman effect, i.e.  $\langle n|L + 2S|n\rangle = 0$  for all  $|n\rangle$ . The calculation of the second-order term is straightforward within tensor operator formalism. We write

$$\langle SLJM|L + 2S|SLJ'M'\rangle = (-1)^{J-M} \begin{pmatrix} J & 1 & J' \\ -M & q & M' \end{pmatrix} \langle SLJ||L + 2S||SLJ'\rangle \quad (5)$$

where the 1 in the  $3-j$  symbol reflects the fact that the rank of the combined-tensor operator  $L + 2S$  is 1. Using the standard relations between the Cartesian and the spherical components for the angular momentum and spin tensors we have

$$\begin{aligned} L_x + 2S_x &= (-1/\sqrt{2})[(L_{+1} + 2S_{+1}) - (L_{-1} + 2S_{-1})] \\ L_y + 2S_y &= (i/\sqrt{2})[(L_{+1} + 2S_{+1}) + (L_{-1} + 2S_{-1})] \\ L_z + 2S_z &= L_0 + 2S_0. \end{aligned} \quad (6)$$

The reduced matrix element in equation (5) can be written as

$$\langle SLJ||L||SLJ'\rangle + 2\langle SLJ||S||SLJ'\rangle$$

and may be further reduced to

$$\langle SLJ||L||SLJ'\rangle = (-1)^{7+J'} [(2J' + 1)(2J + 1)]^{1/2} \left\{ \begin{matrix} J & 1 & J' \\ L & S & L \end{matrix} \right\} \langle SL||L||SL'\rangle \quad (7)$$

with a similar expression for  $\langle SLJ||S||SLJ'\rangle$ . The doubly reduced matrix elements  $\langle SL||L||SL\rangle$  and  $\langle SL||S||SL\rangle$  may then be obtained from the general formula

$$\langle ab||b||ab\rangle = [b(b+1)(2b+1)]^{1/2} \quad (8)$$

with  $b$  denoting either  $L$  or  $S$ . For the special case of  $\text{Eu}^{3+}$  (configuration  $f^6$ ) the  $LS$  ground state is  ${}^7F_0$  and hence  $L = S = 3$  and the values obtained for the doubly reduced matrix elements are the same for both  $L$  and  $S$  operators (cf table 1). All the necessary  $3-j$  and  $6-j$  symbols are given in the tables of Rothenberg *et al* [10]. With the expressions in equation (6) as operators and the wavefunctions in equation (4) it is then possible to calculate the second-order Zeeman matrix elements in equation (5). Inserting the results into equation (1) gives the required results for the molar susceptibilities:

$$\begin{aligned} \chi_M^{(x)} &= D\{(8/E_d)[1 - \text{ex}(d)] \\ &\quad + \frac{9}{2}[1/(E_c - E_b)][\text{ex}(b) - \text{ex}(c)] + [15/(E_e - E_d)] \text{ex}(d)\} \\ \chi_M^{(y)} &= D\{(8/E_c)[1 - \text{ex}(c)] \\ &\quad + \frac{9}{2}[1/(E_d - E_b)][\text{ex}(b) - \text{ex}(d)] + [15/(E_e - E_c)] \text{ex}(c)\} \\ \chi_M^{(z)} &= D\{(8/E_b)[1 - \text{ex}(b)] \\ &\quad + \frac{9}{2}[1/(E_d - E_c)][\text{ex}(c) - \text{ex}(d)] + [15/(E_e - E_b)] \text{ex}(b)\} \end{aligned} \quad (9)$$

where the shorthand notation  $\text{ex}(n)$  is used for the Boltzmann factor  $\exp(-E_n/kT)$ , and the contribution of the second excited state  ${}^7\text{F}_2$  has been included with its free-ion value:

$$[15/(E_e - E_n)] \text{ex}(n) \quad n = b, c, d \quad (10)$$

as an extra term in equation (9).

**Table 1.** Non-vanishing reduced and doubly reduced matrix elements for second-order Zeeman effect in  $\text{Eu}^{3+}$ .

Reduced matrix elements	Doubly reduced matrix elements
$\langle f^6 331    L    f^6 331 \rangle = \sqrt{\frac{3}{2}}$	$\langle f^6 33    L    f^6 33 \rangle = 2\sqrt{21}$
$\langle f^6 331    S    f^6 331 \rangle = \sqrt{\frac{3}{2}}$	$\langle f^6 33    S    f^6 33 \rangle = 2\sqrt{21}$
$\langle f^6 331    L    f^6 330 \rangle = 2\sqrt{3}$	
$\langle f^6 331    S    f^6 330 \rangle = -2\sqrt{3}$	

## 5. Results

In order to compare experimental and calculated molar magnetic susceptibilities it is necessary to estimate the diamagnetic correction. We prefer an empirical method to find this correction rather than using the conventional ionic increment values [11]. For this work the experimentally determined susceptibilities of the diamagnetic compounds  $\text{Cs}_3\text{La}(\text{N}_3)_6$  ( $\chi_M = -2.79 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$ ) and  $\text{CsN}_3$  ( $\chi_M = -0.12 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$ ), taken twice in order to account for the number of  $\text{Cs}^+$  and  $\text{N}_3^-$  ions in  $\text{Cs}_5\text{Eu}(\text{N}_3)_8$ , were employed to obtain the diamagnetic correction for the  $\text{Eu}^{3+}$  compound:

$$\chi_{M,\text{dia}} = -3.03 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}.$$

(The still very common incremental method yields a diamagnetic correction of  $-3.88 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$  which turns out to be inappropriate here.)

Using the model discussed in the previous section the molar magnetic susceptibility of  $\text{Eu}^{3+}$  in  $\text{Cs}_5\text{Eu}(\text{N}_3)_8$  has been calculated in the temperature interval from 77 to 300 K in order to compare it with the experimental data. Figure 2 shows the calculated magnetic susceptibility for the compound using the site I energy levels. The agreement between calculated and experimental data is excellent from room temperature down to about 150 K; very similar results are obtained for the site II energy levels. At lower temperatures, curves calculated for 100% site I or 100% site II begin to deviate from the experimental values.

Figure 3 shows the low-temperature part of the data on an expanded scale. The crystal-field splitting of site I obviously produces data which are too low, whereas site II gives data which are too high compared with the experimental values. However, if one assumes equal proportions of site I and site II in the substance, which is in accordance with the results of the spectroscopic investigation, then there is perfect agreement between experimental and calculated susceptibility data over the whole temperature range (cf figure 3). A representative selection of experimental and calculated susceptibility data is given in table 2.

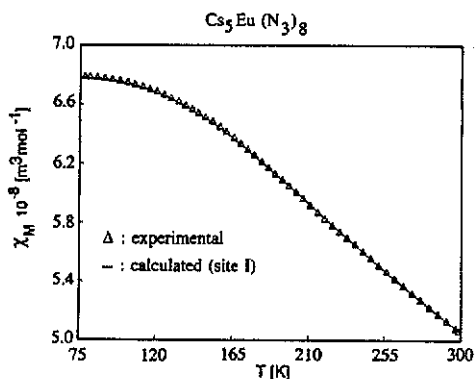


Figure 2. Calculated and experimental temperature dependence of the molar magnetic susceptibility of  $\text{Eu}^{3+}$  in  $\text{Cs}_5\text{Eu}(\text{N}_3)_8$ . The crystal-field energies of site I were used for the calculated curve.

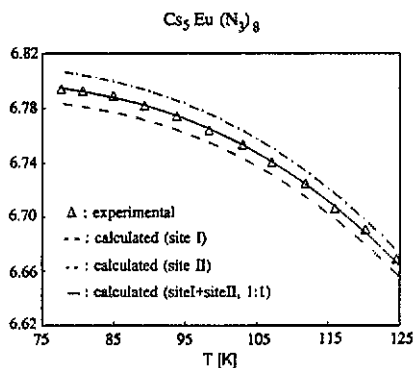


Figure 3. Calculated and experimental temperature dependence of the molar magnetic susceptibility of  $\text{Eu}^{3+}$  in  $\text{Cs}_5\text{Eu}(\text{N}_3)_8$ . The experimental points are averages of five individual runs. The calculated curves are obtained using the site I, site II and site I + site II (1:1) energies.

Table 2. Experimental and calculated magnetic susceptibilities at different temperatures. The calculated data are obtained for equal amounts of sites I and II.

$T$ (K)	$\chi_{M,\text{exp}}$ ( $10^8 \text{ m}^3 \text{ mol}^{-1}$ )	$\chi_{M,\text{calc}}$ ( $10^8 \text{ m}^3 \text{ mol}^{-1}$ )
298.5	5.066	5.067
276.2	5.272	5.269
251.6	5.510	5.507
228.4	5.739	5.742
202.7	6.008	6.007
177.7	6.261	6.257
157.4	6.446	6.440
133.0	6.623	6.619
111.8	6.725	6.724
93.8	6.774	6.775
77.6	6.795	6.795

## 6. Conclusions

It has been shown that the magnetic susceptibility of the complex rare-earth azide  $\text{Cs}_5\text{Eu}(\text{N}_3)_8$  can be described adequately by the Van Vleck model for closely spaced multiplets. In addition, measurement of the temperature dependence of the magnetic susceptibility has proven to be a highly sensitive tool for discriminating between different microsymmetries around the central  $\text{Eu}^{3+}$  ions in this material. It must be emphasized that the difference in the crystal-field splitting of the two sites is very small, amounting to a few wavenumbers only. It is evident from the last line of equation (9) that the sensitivity of the employed model for such small energy differences lies mainly in the denominator  $E_d - E_c$  of  $\chi^{(z)}$ . Hence the deviation from  $D_{4d}$  symmetry which causes a small splitting of the otherwise degenerate  $E_1$  state arising from the  ${}^7F_1$  multiplet makes this term the most important contribution to the magnetic susceptibility. Since this splitting is slightly different for both sites, their susceptibility becomes measurably different. It turns out that, in this case, magnetic susceptibility data are a reliable and valuable complementation of the data found with high-resolution spectroscopy techniques.

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