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On the hyperfine interaction in rare-earth Van Vleck paramagnets at high magnetic fields

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Abstract

The influence of high magnetic fields on the hyperfine interaction in rare-earth ions with a non-magnetic ground state (Van Vleck ions) is investigated theoretically for the case of Tm^{3+} ions in an axially symmetrical crystal electric field (in an ethylsulphate crystal). It is shown that magnetic-field-induced distortions of the 4f-electron shell lead to crucial changes in the hyperfine magnetic field at the nucleus. The proposed theoretical model is in agreement with recent experimental data.

1. Introduction

The Van Vleck (VV) or polarization magnetism most often occurs in crystals containing non-Kramers rare-earth (RE) ions, i.e. ions with even numbers of electrons in the unfilled 4f shell, where the crystalline electric field lifts the degeneracy of the ground multiplet $^{2S+1}L_J$, leading to typical splittings of the Stark structure of the order of 10–100 cm^{-1}. The electronic ground state in this case is a singlet or non-magnetic doublet, so all magnetic properties of VV paramagnets necessarily arise from the Zeeman effect which at moderate magnetic fields (the Zeeman energy is much less than the Stark splittings) can be calculated in the second order of perturbation theory [1–3]. The rather strong hyperfine interaction induces a magnetic field at the nucleus of the VV ion that is many times greater than the applied external magnetic field and this leads to enormous magnitudes (by factors of up to several hundred) of the paramagnetic shifts for the NMR lines. This so-called 'enhanced' NMR is one of the most important tools for use in studying the magnetic properties of VV paramagnets [2, 3].

At high magnetic fields the Zeeman energy of the RE ion becomes comparable with the Stark splitting energies and a number of new physical effects appear [4]. Among them, the magnetic-field-induced structural phase transitions in the dielectric VV paramagnets

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$TmPO_4$ [5] and $LiTmF_4$ [6] and the coupled 4f-electron–phonon excitations in the thulium ethylsulphate crystal $Tm(C_2H_5SO_4)_2{\cdot}9H_2O$ (TmES) [7] might be mentioned. From the theoretical point of view, perturbation theory is no longer applicable at high magnetic fields and a new theory has to be built up [4, 8]. For example, it was shown in [4, 9] that at high magnetic fields, coupled 4f-electron–nuclear states appear in insulating VV paramagnets. Resonant absorption due to the transitions between electron–nuclear sublevels of the ground singlet in TmES crystal was observed in [10] at magnetic fields up to 3 T. It should be pointed out that the frequencies of those transitions lie almost in the X band of the EPR frequencies, while the transition probabilities are determined by the matrix elements of the nuclear spin operator. From this point of view it is reasonable to speak about 'ultrahigh-frequency' NMR at high magnetic field, in contrast to the 'enhanced' NMR at moderate magnetic fields. The observed field dependence of the transition frequencies does not coincide with that predicted in [4, 9], where for clarity in setting out the essential changes arising in properties of the nuclear spin system of an insulating VV paramagnet under the influence of a high magnetic field the possible changes in the hyperfine interaction parameters were neglected. But a sufficiently high magnetic field will cause distortion of the 4f-electron shell and a redistribution of the electron density, inevitably altering the hyperfine field at the nucleus.

In this paper, we investigate theoretically the influence of a rather high external magnetic field on the hyperfine interaction in dielectric VV paramagnets. As a model system, the TmES crystal, well studied at moderate magnetic fields, is considered.

2. Hyperfine interaction in VV paramagnets

The Hamiltonian of an isolated VV ion (the distance between two nearest-neighbour thulium ions in TmES is ∼7 Å and the single-ion approximation works rather well) can be written as

$$\mathcal{H} = \mathcal{H}_{cr} + \mathcal{H}_{eZ} + \mathcal{H}_{nZ} + \mathcal{H}_{hf}, \tag{1}$$

where the crystal-electric-field Hamiltonian in generally accepted notation [11] reads as

$$\mathcal{H}_{cr} = \alpha B_{20} O_2^0 + \beta B_{40} O_4^0 + \gamma (B_{60} O_6^0 + B_{66} O_6^6). \tag{2}$$

The Hamiltonian of the Zeeman interaction of the 4f-electron shell and that of the nuclear Zeeman interaction are, in the usual forms,

$$\mathcal{H}_{eZ} = g_J \mu_B \boldsymbol{H} \cdot \boldsymbol{J}, \qquad \mathcal{H}_{nZ} = -\gamma_I \hbar \boldsymbol{H} \cdot \boldsymbol{I}. \tag{3}$$

The explicit form of the Hamiltonian of the hyperfine interaction $\mathcal{H}_{hf}$ can be estimated in the case of RE ions in the following way (see, for example, [11]; note that we shall not consider hereinafter quadrupole effects because the ^{169}Tm nuclear spin is one half). For a free RE the magnetic interaction with the nucleus of the electrons in the partially filled 4f shell with orbital moments $\boldsymbol{l}_i$ and spins $\boldsymbol{s}_i$ is given by

$$\mathcal{H}_{hf} = 2\mu_B \gamma_I \hbar \sum_{i \in 4f} \{r_i^{-3}[\boldsymbol{l}_i - \boldsymbol{s}_i + 3\boldsymbol{r}_i(\boldsymbol{r}_i \cdot \boldsymbol{s}_i)/r_i^2]\} \cdot \boldsymbol{I} = 2\mu_B \gamma_I \hbar \langle r_i^{-3} \rangle (\boldsymbol{N} \cdot \boldsymbol{I}) \tag{4}$$

and can be represented within the ground multiplet manifold $^{2S+1}L_J$ where the total angular momentum $\boldsymbol{J}$ is a good quantum number as

$$\mathcal{H}_{hf} = 2\mu_B \gamma_I \hbar \langle r_i^{-3} \rangle \langle J \| N \| J \rangle (\boldsymbol{J} \cdot \boldsymbol{I}) = A_{hf} (\boldsymbol{J} \cdot \boldsymbol{I}). \tag{5}$$

The reduced matrix elements $\langle J \| N \| J \rangle$ have been tabulated for different $4f^n$ electronic configurations [11].

For an RE ion in a crystal the crystal electric field reduces the rotational symmetry of the free atom and removes partially or completely the degeneracies of the energy levels. As a result,

asymmetry reflecting the local environment symmetry of an RE ion appears in the hyperfine interaction parameter A_{hf}. So equation (5) has to be replaced by

$$\mathcal{H}_{hf} = (\boldsymbol{J}\tilde{A}\boldsymbol{I}). \tag{6}$$

For example, in the ethylsulphates of RE ions with magnetic ground states (electronic levels exhibit the Kramers degeneracy), the principal values of the hyperfine interaction tensor $\tilde{A}$ obtained by measurements of the hyperfine structure of the paramagnetic resonance lines can differ by factors of 10 or more. But for VV ions, i.e. non-Kramers ions with a non-magnetic ground state such as Tm^{3+} in TmES (the total angular momentum is quenched by the crystal electric field), the paramagnetic resonance is not observable and the principal values of $\tilde{A}$ are determined in an indirect way. For our estimations we have used the value measured by means of the enhanced NMR at moderate magnetic fields. It is the so-called paramagnetic shift [12] which is anisotropic and its values depend on the strength of the hyperfine interaction as well as on the degree of mixing of the Stark wavefunctions by the applied magnetic field. Taking into account the explicit form of the wavefunctions for the Hamiltonian $\mathcal{H}_{cr} + \mathcal{H}_{eZ}$, we get after calculations the following principal values of the hyperfine interaction tensor for Tm^{3+} in the axial crystal field in TmES: $A_{\parallel} \approx -241$ MHz and $A_{\perp} \approx -388$ MHz (the estimated value of A_{hf} for the free tripositive ion Tm^{3+}, from measurements on Tm and Tm^{2+}, is -393.5 MHz [11]).

A rather high magnetic field in which the Zeeman energy is comparable with the Stark splittings of the ground multiplet leads to further lowering of the symmetry and consequently to redistribution of the 4f-electron density in VV ions (see figure 1(a) where we show the influence of the magnetic field 5 T on the angular distribution of the 4f-electron density; note that most of the distortion occurs along the applied magnetic field direction because of the nature of the polarization of the VV paramagnetism). The inclusion of such a magnetic field can be considered formally as the appearance of a low-symmetry magnetic-field-dependent term in the crystal-field Hamiltonian. Consequently, we can assume that the magnetic hyperfine interaction is still described by equation (6) where the components of the hyperfine interaction tensor $\tilde{A}$ depend on the strength of the applied magnetic field. It was shown in [8] that in the case of the TmES compound, magnetic fields above $\sim$5 T cause observable changes in the structure of the electronic energy levels (see also [4]). But the recent ultrahigh-frequency ^{169}Tm NMR experiments on TmES [10] are believed to demonstrate that even below 5 T the redistribution of the 4f-electron density leads to significant changes in the hyperfine interaction (see figure 1(b) and its caption).

To our knowledge, *ab initio* calculations of crystal-field effects and magnetic properties have not been provided for the VV paramagnets yet. So in order to estimate theoretical values of hyperfine interaction parameters for insulating VV paramagnets at high magnetic field and to compare the results obtained with the magnetic field dependence of the resonant frequencies due to transitions between electron–nuclear states in TmES observed in [10], the following phenomenological model can be proposed. Assuming that the external magnetic field is not so high as to destroy partially the LS-coupling and taking into account that the hyperfine magnetic field at the nucleus is determined by the magnetic moment of the 4f-electron shell, one can write for the principal values of the hyperfine interaction tensor at high magnetic field the following relation:

$$\frac{A_{\parallel,\perp}(H)}{M_{\parallel,\perp}(H)} = \frac{A_{\parallel,\perp}}{M_{\parallel,\perp}}, \tag{7}$$

where $M_{\parallel,\perp}(H)$ and $M_{\parallel,\perp}$ represent the components of the electronic magnetic moment of the Tm^{3+} ion at high magnetic field and moderate magnetic field, respectively, and can be

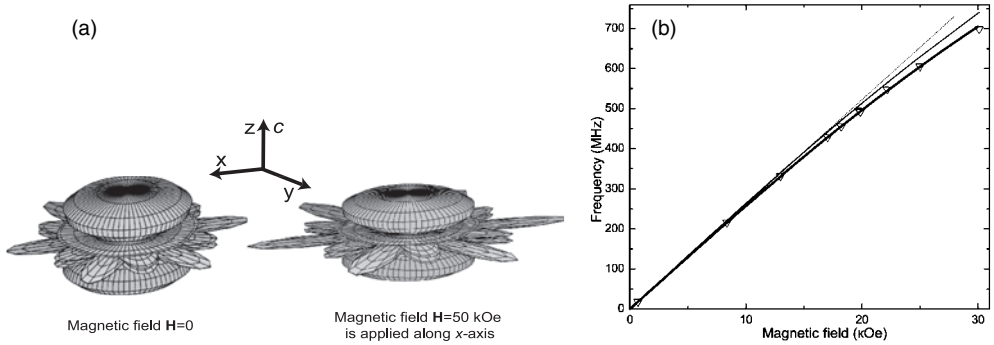

Figure 1. (a) The angular distribution of the 4f-electron density in TmES in the absence of an applied magnetic field and in a field of 5 T. (b) Magnetic field dependences of the frequencies of transitions between the Tm^{3+} ground state electron–nuclear sublevels in TmES at 4.2 K: $\triangledown$ are the experimental points from [10]; the dashed curve shows the results from the enhanced NMR theory [3]; the thin curve shows the high-magnetic-field calculations without taking into account the change in the hyperfine interaction parameters [4]; and the thick curve shows the present theoretical calculations.

calculated by use of the wavefunctions of the Hamiltonian $\mathcal{H}_{cr} + \mathcal{H}_{eZ}$. The principal values $A_{\parallel,\perp}$ have been determined above. The background for using such a model is the polarization nature of the VV paramagnetism. Note also here that because of the dependence of the 4f-electron magnetic moment in VV paramagnets on the populations of the nearest excited levels at temperatures above $\sim$10 K [7], the temperature dependence of the hyperfine interaction parameters could be expected. The calculations made using the above model allowed us to describe the observed experimental data [10] well (the thick curve in figure 1(b)).

3. Summary

In summary, we have shown that at rather high magnetic field, where the Zeeman energy of a VV ion is comparable with the Stark structure splitting energies, the components of the magnetic hyperfine interaction tensor begin to be dependent on the applied magnetic field strength. A phenomenological model that can be used for taking into account the influence of the induced external magnetic field distortions of the 4f-electron shell on the hyperfine magnetic field at the nucleus in insulating VV paramagnets has been proposed. The results of these studies can be applied also to intermetallic VV paramagnets, which are very interesting from the point of view of ultralow-temperature physics.

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References

[1] Van Vleck J H 1929 *Phys. Rev.* **34** 1494
[2] Abragam A and Bleaney B 1983 *Proc. R. Soc.* A **387** 221
[3] Aminov L K and Teplov M A 1985 *Sov. Phys.–Usp.* **28** 762
Aminov L K and Teplov M A 1990 *Sov. Sci. Rev.* A **14** 1 and references therein

[4] Tagirov M S and Tayurskii D A 2002 *Low Temp. Phys.* **28** 147
[5] Vekhter B G *et al* 1991 *JETP Lett.* **54** 578
[6] Klochkov A V *et al* 1997 *JETP Lett.* **66** 266
[7] Tayurskii D A and Tagirov M S 1998 *JETP Lett.* **67** 1040
[8] Tagirov M S and Tayurskii D A 1995 *JETP Lett.* **61** 672
[9] Tayurskii D A *et al* 2000 *Physica* B **284–288** 1686
[10] Abubakirov D I *et al* 2002 *JETP Lett.* **76** 633
[11] Abragam A and Bleaney B 1970 *Electron Paramagnetic Resonance of Transition Ions* (Oxford: Clarendon)
[12] Abdulsabirov R Yu *et al* 1979 *Sov. Phys.–JETP* **49** 517