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Anisotropic magnetic susceptibility and crystal field analysis in the Van Vleck paramagnet PrF_3

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Abstract

The magnetic susceptibility of PrF_3 was measured in an external magnetic field of 0.01 T directed across and along the crystallographic c -axis at temperatures in the range 2–300 K. The maximum values of the measured susceptibilities (less than 1.2×10^{-4} emu g^{-1}) are consistent with the expected pattern of non-degenerate energy levels of the electronic $4f^2$ configuration in the low-symmetry crystal field. The longitudinal susceptibility decreases monotonically with the temperature increase while the transversal susceptibility has a broad maximum at 60 K. A crystal field analysis based on the magnetic susceptibility data and calculations in the framework of the exchange charge model was carried out. The set of crystal field parameters related to the crystallographic system of coordinates has been obtained and used to reproduce successfully the temperature dependences of the longitudinal and transversal components of the susceptibility tensor and the crystal field energies, as well as the parameters of the effective spin Hamiltonian of the ^{141}Pr nuclei.

1. Introduction

The magnetic properties of rare-earth trifluorides RF_3 with the tysonite structure have been the subject of quite a few studies in the past. Special attention has been attracted to LaF_3 crystals doped with R^{3+} rare-earth ions due to the important technical application of the $\text{LaF}_3:\text{R}^{3+}$ as laser materials. Consequently, the optical data on a large number of R^{3+} ions in LaF_3 have been reported (see the references in [1, 2]). Several rather successful attempts have been made to calculate the energy levels and eigenfunctions of impurity rare-earth ions in the LaF_3 host, and to determine the crystal field parameters using models of various degrees of

sophistication [1, 3]. However, up to now, scant information exists on the energy level schemes and crystal field parameters of rare-earth ions in concentrated RF_3 crystals including PrF_3 .

At the present time interest in the Van Vleck paramagnet praseodymium trifluoride has been rekindled for several reasons. First, the magnetic ordering of the ^{141}Pr nuclear moments would be realized at ultra-low temperatures in this compound. The ordering temperature was estimated to be about 0.1 mK [4]. Knowledge of the parameters of the crystal field affecting Pr^{3+} ions is a prerequisite for creating any theory describing this phenomenon. Second, it was shown that solid Van Vleck paramagnets might be used for the dynamic polarization of ^3He nuclei in the liquid helium by means of the so-called 'solid effect' method [5]. Recent NMR investigations of the magnetic coupling between the ^{141}Pr and ^3He nuclei in the system 'solid PrF_3 –liquid ^3He ' and studies of the surface quality of PrF_3 particles of different size in powders suggest this Van Vleck paramagnet as a promising material for the dynamic polarization of ^3He nuclei [6]. Practical realization of this task requires knowledge of the crystal field parameters of PrF_3 related to the crystallographic system of coordinates and the energy level pattern of the ground multiplet at high magnetic fields.

Investigations of the electronic energy levels of the Pr^{3+} ion in PrF_3 were performed making use of Raman and fluorescence spectroscopy [7, 8], infrared absorption spectroscopy [8, 9], and inelastic neutron scattering [10]. The ground multiplet $^3\text{H}_4$ gave rise to nine electronic energy levels ($2J + 1 = 9$) in the low-symmetry crystal field. However, the results of the studies at high magnetic fields up to 8 T showed the number of energy levels to be up to sixteen. It has been proved that these surplus levels are not due to Pr^{3+} ions in distorted positions or other rare-earth impurities but are an inherent property of the bulk crystal [8, 11]. An intrinsic explanation for the electronic spectrum with extra energy levels is the Davydov splitting caused by interactions between the Pr^{3+} ions [8, 11]. Investigations of the higher multiplets have not revealed any anomaly. Schaack and Dahl [7] determined a set of crystal field parameters which allowed them to obtain a rather good agreement between the calculated and experimental crystal field energies for the higher multiplets; however, the model failed to explain the energy level scheme of the $^3\text{H}_4$ multiplet known from Raman scattering and infrared absorption measurements.

The magnetic susceptibility of a rare-earth paramagnet mainly depends on the excitation energies and wavefunctions of the crystal field sublevels of the lowest multiplet. The magnetic susceptibility of the PrF_3 single crystal measured in a magnetic field applied along the c -axis at temperatures in the range 2–300 K is reported in [12]; however, the data obtained were not analysed in the framework of crystal field theory. Parameters of the effective nuclear spin Hamiltonian of ^{141}Pr (the nuclear spin $I = 5/2$) in LaF_3 and PrF_3 were measured by nuclear magnetic resonance and reported in [13, 14]. None of the published sets of the crystal field parameters satisfactorily fitted the components of the enhanced nuclear g -factor and the electric field gradient at the ^{141}Pr nucleus [13].

In the present study the temperature dependences of the principal values of the magnetic susceptibility tensor in PrF_3 were obtained from direct measurements with a SQUID magnetometer. The set of crystal field parameters for the Pr^{3+} ions related to the fixed local systems of coordinates in Pr^{3+} sites with the C_2 symmetry in the crystal lattice with the tysonite structure has been obtained from the fitting of calculated susceptibilities to the measured data and the subsequent comparison of the calculated crystal field energies with the data available from the literature. The final results of the fitting procedure are close to estimates of the crystal field parameters in the framework of the semi-phenomenological exchange charge model [15]. A good agreement between the calculated and previously measured parameters of the nuclear spin Hamiltonian confirms the physical meaning of the crystal field parameters obtained in this work.

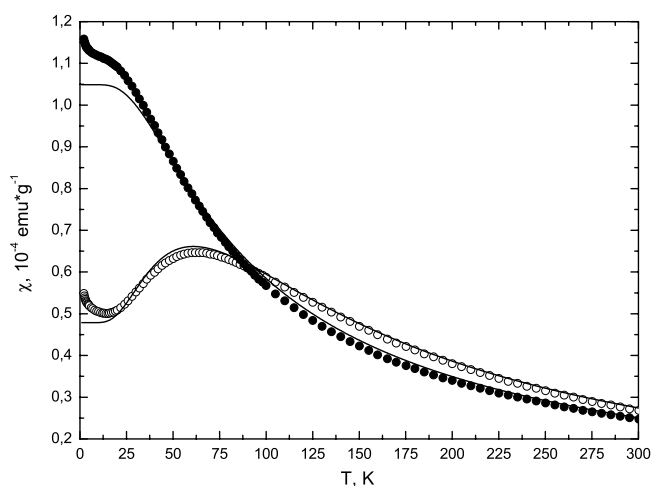


Figure 1. Magnetic susceptibilities of PrF₃ measured in an external magnetic field of 0.01 T directed across (solid circles) and along (open circles) the *c*-axis. Solid curves represent results of simulations.

2. Experimental results

A PrF₃ single crystal was grown by the Bridgman–Stockbarger method in carbon crucibles in an atmosphere of high purity argon from PrF₃ powder at the melting temperature of 1400 °C under a pressure of 20 kPa. Additionally, the atmosphere was fluorinated by burning tetrafluoroethylene. EPR measurements have shown that the paramagnetic admixture content (Er³⁺, Dy³⁺, Nd³⁺, Gd³⁺ and Sm³⁺ ions) in total differs by much less than 0.01% from the number of Pr³⁺ ions. A dc SQUID magnetometer MPSM (Quantum Design) was used for measurements of the magnetic susceptibility. The sample was oriented using an x-ray diffraction pattern with an accuracy of ±3°.

The results of susceptibility measurements in a PrF₃ single crystal from 2 K up to 300 K are presented in figure 1. A magnetic field of 0.01 T was applied across and along the crystallographic *c*-axis. PrF₃ crystal is a Van Vleck paramagnet with a gap between the ground and the first excited electronic singlet states of Pr³⁺ ions larger than 80 K [7]. One might expect to observe temperature-independent magnetic susceptibility in the 2–16 K temperature range [12]. However, anomalous behavior of the susceptibilities is actually observed in this temperature range, resembling a paramagnetic contribution. This anomaly is not due to any admixtures of other rare-earth ions (Er³⁺, Dy³⁺, Nd³⁺, Gd³⁺, and Sm³⁺) because in this case the content of the paramagnetic ions must differ by at least 0.05% from the number of Pr³⁺ ions contrary to the EPR data mentioned above. We suggest that this anomaly arises from intrinsic lattice defects in PrF₃. Local crystal fields in the region of the defects differ from the crystal field in the ‘bulk’. As a result, a quasi-doublet crystal field state may appear as the ground state of a Pr³⁺ ion. Similar lattice defects were found in the near-surface layer of the LiTmF₄ particles in powders [16]. The observed temperature-dependent paramagnetic contributions do not vary with the direction of the magnetic field at low temperatures and disappear at high magnetic fields (they completely disappear in the fields higher than 5.5 T). These facts are consistent with the presence of Pr³⁺ ions in randomly deformed coordination shells: the effective electronic *g*-factor of the Pr³⁺ ion in the strong axial field may be close to 6, and the corresponding splitting of the quasi-doublet in the magnetic field 5.5 T exceeds 20 K.

3. Crystal field Hamiltonian and the susceptibility tensor

The Pr^{3+} ions occupy six homologous sites per unit cell of PrF_3 . For a long time, there was no commonly accepted agreement on the space group of RF_3 and for PrF_3 as well. Mansmann [17] proposed a trigonal structure with the space group D_{3d}^4 from x-ray investigations. An elementary cell of this structure contains six formula units. Gregson and co-authors [18] reported a non-centrosymmetric structure with the space group C_{6v}^3 also containing six formula units from elastic neutron scattering experiments. These structures differ from each other only in the positions of the F1 (fluorine) ion. The site symmetry of the rare-earth ion is C_2 for D_{3d}^4 and C_s for C_{6v}^3 . Also the possibility of a twinned crystal structure with the space group D_{3d}^4 for the domains was discussed by Anderson and Johansson [19]. Dahl and Schaack [7] considered both possible types of the crystal field symmetry (C_2 and C_s) for the Pr^{3+} ion in the PrF_3 crystal lattice. They obtained crystal field parameters for C_2 and C_s symmetry with almost the same rms deviations for the energy levels of the multiplets higher than ${}^3\text{H}_4$. At present, the PrF_3 crystal lattice with the twinned trigonal D_{3d}^4 structure is favoured [13, 20, 21].

We have calculated the magnetic susceptibility of the paramagnetic crystal PrF_3 in the framework of the single-ion approximation. The Hamiltonian of the Pr^{3+} ion in the external magnetic field \vec{H}_0 , acting within the space of 91 states of the ground $4f^2$ electronic configuration,

$$H = H_{\text{fi}} + H_{\text{cf}} + H_Z \quad (1)$$

contains the free ion Hamiltonian H_{fi} which involves energies of electrostatic and spin-orbit interactions, the crystal field Hamiltonian H_{cf} and the Zeeman Hamiltonian $H_Z = -\vec{\mu}\vec{H}_0$, where

$$\vec{\mu} = -\mu_B \sum_{i=1,2} (\vec{l}_i + 2\vec{s}_i) \quad (2)$$

is the magnetic moment operator of an ion, μ_B is the Bohr magneton, and \vec{l}_i and \vec{s}_i are the one-electron orbital and spin moments, respectively. The free ion parameters for the Pr^{3+} ion were taken from the paper by Carnall *et al* [22] (in units of cm^{-1} , the Racah parameters $E_1 = 4548.2$; $E_2 = 21.937$; $E_3 = 466.73$; the spin-orbit coupling constant $\zeta = 740.75$; the Trees parameters $\alpha = 21.255$; $\beta = -800$; $\gamma = 1343$).

The crystal fields affecting the Pr^{3+} ions in the six sites within the unit cell of the PrF_3 crystal lattice differ only by their orientations. In the local coordinate system with the z -axis parallel to the corresponding symmetry axis C_2 , the crystal field Hamiltonian is given by the expression

$$H_{\text{cf}} = \sum_{k,q} B_{kq} C_{kq}; \quad k = 2, 4, 6; \quad q = -k, -k+2, \dots, k-2, k, \quad (3)$$

where C_{kq} are the components of a spherical tensor of rank k , and B_{kq} are the complex crystal field parameters ($B_{k,-|q|} = (-1)^q B_{k|q|}^*$) which describe the effect of the crystal field on the free ion energy levels. The Hamiltonian (3) contains 15 independent parameters. However, in the absence of information about the eigenfunctions of the crystal field Hamiltonian, it is impossible to find all 15 crystal field parameters from studies of the energy spectrum of a paramagnetic ion (in particular, from optical absorption, fluorescence and Raman spectroscopy data). Rotation of a local coordinate system around the symmetry axis by any angle φ does not change the structure of the crystal field Hamiltonian. The B'_{kq} parameters in the transformed system of coordinates are related to the B_{kq} parameters by the following expressions:

$$\begin{aligned} \text{Re } B'_{kq} &= \text{Re } B_{kq} \cdot \cos q\varphi + \text{Im } B_{kq} \cdot \sin q\varphi, \\ \text{Im } B'_{kq} &= -\text{Re } B_{kq} \cdot \sin q\varphi + \text{Im } B_{kq} \cdot \cos q\varphi. \end{aligned} \quad (4)$$

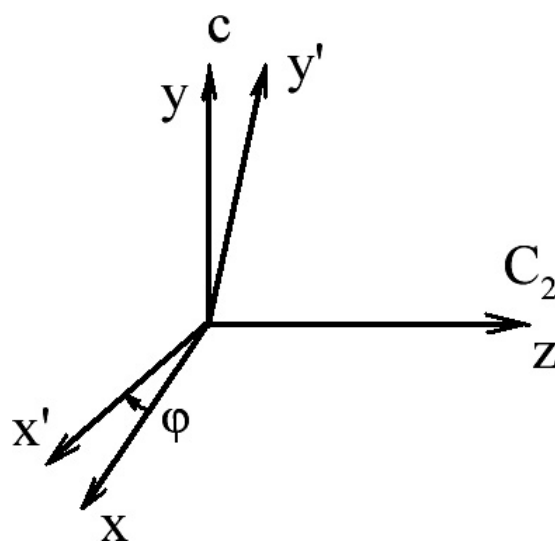


Figure 2. Local coordinate system of the Pr³⁺ ion in PrF₃.

So, there is an infinite number of different sets of crystal field parameters connected by transformations (4) which bring about the same eigenvalues of the crystal field Hamiltonian (3). To avoid ambiguity in the determination of the crystal field parameters, their number is usually reduced by the rotation, which removes, in particular, $\text{Im } B_{22}$ or $\text{Im } B_{66}$ [7, 10]. Thus, the number of the independent B_{kq} parameters is reduced by one to 14. However, the orientations of the x' and y' axes of the local coordinate system relative to the crystallographic axes remain unknown (see figure 2).

Morrison and Leavitt [1] obtained 14 crystal field parameters B_{kq} ($\text{Im } B_{22} = 0$) for the impurity Pr³⁺ ions in the LaF₃ crystal isomorphic to PrF₃ from the analysis of the optical spectra (see table 1). The authors started from a point-charge model and used the atomic positions given by Cheetham *et al* [23] to calculate starting values of parameters. The crystal field energies of the Pr³⁺ ion in LaF₃ calculated with this set of the crystal field parameters and the free ion parameters from [22] agree satisfactorily with the experimental data for the excited multiplets of the electronic 4f² configuration, and for the ground state ³H₄ as well. However, we cannot use these parameters directly to analyse the crystal field and magnetic properties of PrF₃ because of the different lattice structure constants (the unit cell dimensions and the basis vectors) of PrF₃ and LaF₃ [24]. Moreover, to write the Zeeman energy correctly, we have to define the external magnetic field components relative to the fixed local system of coordinates. So, we will use the local coordinate systems with the z -axes along the C₂ symmetry axes and the y -axes along the c -axis of the crystal lattice (see figure 2). These coordinate systems may be regarded as a result of rotations by an angle φ around the C₂ axes of coordinate systems related to the set of the crystal field parameters determined by Morrison and Leavitt.

In a case of non-degenerate crystal field states of a paramagnetic ion, the single-ion magnetic susceptibility tensor is defined as

$$\chi_{\alpha\beta} = - \sum_{k,l} \frac{\langle k|\mu_{\alpha}|l\rangle\langle l|\mu_{\beta}|k\rangle + \langle k|\mu_{\beta}|l\rangle\langle l|\mu_{\alpha}|k\rangle}{E_k - E_l} \frac{\exp(-E_k/kT)}{\sum_p \exp(-E_p/kT)}, \quad (5)$$

where E_k and $|k\rangle$ are the eigenvalues and eigenfunctions of the Hamiltonian (1) for the zero external magnetic field, and the fraction on the right-hand side of equation (5) is the relative population of the state k ($k = 1 \dots 91$) at the temperature T .

Table 1. Crystal field parameters B_{kq} (cm^{-1}) for the Pr^{3+} ion in LaF_3 and PrF_3 (the real and imaginary parts are labelled by Re and Im, respectively).

k, q	PrF_3			
	$\text{LaF}_3:\text{Pr}$ [1]	Experimental		
		$(\varphi = 7^\circ)$	Calculated	Experimental
1	2	3	4	5
20	-120	-142	-150	-167.5
22	-98	-67	-22	-40.3
22 Im	0	17	-12	-12.5
40	644	654	643	637.5
42 Re	375	354	445	428
42 Im	123	33.5	133	135
44 Re	483	644	456	489
44 Im	343	59	250	259
60	503	534	610	612
62 Re	-1000	-1052	-976	-1006
62 Im	78	340	71	70
64 Re	-131	-340	-159	-155
64 Im	-509	-371	-473	-452
66 Re	-381	-857	-545	-533
66 Im	-608	-212	-646	-652

The susceptibility tensor of PrF_3 is diagonal; its elements can be expressed through the single-ion susceptibilities (5) as follows:

$$\chi_{\parallel} = \frac{N_A}{M} \chi_{yy}, \quad \chi_{\perp} = \frac{N_A}{M} \frac{\chi_{xx} + \chi_{zz}}{2}. \quad (6)$$

Here N_A is the Avogadro number, and M is the PrF_3 mass number. When writing equation (6), we have taken into account that the unit cell of PrF_3 contains two regular triangles of Pr^{3+} ions; the local z -axes for these ions are normal to the crystallographic c -axis (y -axis of the local coordinate system) and are connected by $n\pi/3$ ($n = 0, 1, \dots, 5$) rotations around the c -axis. So, all the six Pr^{3+} ions are magnetically equivalent in the magnetic field directed along the c -axis. At low values of the external magnetic field, the elements of the susceptibility tensor equal

$$\chi_{\parallel}^{\text{exp}} = \frac{m_{\parallel}}{M_s H_{0c}}, \quad \chi_{\perp}^{\text{exp}} = \frac{m_{\perp}}{M_s H_{0\perp}} \quad (7)$$

where M_s is the sample mass, and m_{\parallel} and m_{\perp} are the measured values of the magnetic moments in the external magnetic fields H_{0c} and $H_{0\perp}$, respectively.

In order to find the crystal field parameters B_{kq} for the Pr^{3+} ion in PrF_3 , the following fitting function was minimized:

$$\delta = \sum_i [(\chi_{\parallel}(B_{kq}, \varphi, T_i) - \chi_{\parallel}^{\text{exp}}(T_i))^2 + \chi_{\perp}(B_{kq}, \varphi, T_i) - \chi_{\perp}^{\text{exp}}(T_i)]^2 \quad (8)$$

where $\chi_{\perp}(T_i)$, $\chi_{\parallel}(T_i)$ are the experimental values of susceptibilities measured in the applied magnetic field directed across and along the c -axis of the PrF_3 crystal, respectively, and $\chi_{\perp}(B_{kq}, \varphi, T_i)$, $\chi_{\parallel}(B_{kq}, \varphi, T_i)$ are the values of susceptibilities calculated with a current set of crystal field parameters B_{kq} and an angle φ at the temperature T_i .

The fitting procedure involved a search for a set of parameters B_{kq} which would bring about the best description of the measured susceptibilities. The crystal field energies of the

Pr³⁺ ions in the LaF₃ host calculated with the set of parameters of Morrison and Leavitt are in a good agreement with the experimental values. The crystal structures of PrF₃ and LaF₃:Pr³⁺ are only slightly different from each other; consequently we suggested that the crystal field parameters of PrF₃ are rather similar to the parameters of LaF₃:Pr³⁺. In accordance with this suggestion, we used the parameters of Morrison and Leavitt (table 1) transformed by means of a rotation of the system of coordinates about the quantization axis C₂ by an angle φ as starting values in the fitting procedure. A current set of the parameters B_{kq} was obtained randomly in the range of 30% of the starting values. Then magnetic susceptibility curves of PrF₃ were calculated for both directions of the magnetic field (across and along the crystallographic c -axis). The value of the fitting function obtained from equation (8) was compared with the value of this function corresponding to the previous set of crystal field parameters. Of course, this procedure cannot result in exact values of the crystal field parameters corresponding to a minimum of the function δ ; however, the procedure enables us to approach the minimum after a large number of iterations.

It was found that the measured magnetic susceptibilities could be fitted satisfactorily only within a rather narrow range of variations of the angle φ . The parameters obtained were tested additionally by a comparison of calculated crystal field energies with the data of spectroscopic measurements from [7, 8]. A rather good agreement with all experimental data (the temperature dependences of magnetic susceptibilities and the crystal field energies of the ground multiplet) was found within the angular range $\varphi \sim 5^\circ\text{--}8^\circ$. The best fit was obtained for $\varphi \approx 7^\circ$ (see table 1, column 3). As the next step of the fitting procedure, the crystal field parameters obtained for the best fit were compared with the results of calculations in the framework of the exchange charge model (table 1, column 4).

The crystal field parameters

$$B_{kq} = \sum_L e^2 [-Z_L(1 - \sigma)\langle r^k \rangle + \frac{2(2k+1)}{7} R_L^k S_k(R_L)] (-1)^q C_{k-q}(\vartheta_L \varphi_L) / R_L^{k+1} \quad (9)$$

were calculated for the Pr³⁺ ion with the crystallographic coordinates ($ap; 0; c/4$) (the PrF₃ lattice constants are $a = 0.7075$ nm, $c = 0.7234$ nm, $p = 0.6592$ [24]). The same parameters describe the crystal fields acting on the Pr³⁺ ions at the sites ($-ap; -ap; c/4$), ($0; -ap; c/4$) with the local coordinate systems rotated by $2\pi/3$ and $4\pi/3$, respectively, around the c -axis; at the three other sites with the local coordinate systems rotated by $\pi/3$, π and $5\pi/3$, the crystal fields are described by the same complex conjugated parameters. In equation (9) the sum is taken over lattice ions L with charges eZ_L and spherical coordinates ($R_L \vartheta_L \varphi_L$) relative to the rare-earth ion at the origin; σ_k are the shielding constants, $\langle r^k \rangle$ are the moments of the 4f electron charge density, and the exchange charges are defined by the overlap integrals between the wavefunctions of the rare-earth ($|4f, l_z\rangle$) and ligand ($|nl_z\rangle$) ions (we take into account only the outer closed 2s² and 2p⁶ electronic shells of F⁻ ions) [15]:

$$\begin{aligned} S_k(R_L) &= G_s S_s^2(R_L) + G_\sigma S_\sigma^2(R_L) + \gamma_k G_\pi S_\pi^2(R_L), \\ S_s &= \langle 4f0|2s0\rangle, \quad S_\sigma = \langle 4f0|2p0\rangle, \quad S_\pi = \langle 4f1|2p1\rangle, \\ \gamma_2 &= -\gamma_6 = 3/2, \quad \gamma_4 = 1/3. \end{aligned} \quad (10)$$

Calculations were carried out with $\sigma_2 = 0.745$, $\sigma_4 = \sigma_6 = 0$ [25], $\langle r^2 \rangle = 1.086$, $\langle r^4 \rangle = 2.822$, $\langle r^6 \rangle = 15.726$ (atomic units) [26]; the lattice sums were computed by the Ewald method, and the dependences of the overlap integrals (computed with the radial wavefunctions from [26, 27]) on the distance R (in ångströms) between the ions were approximated by functions $S_0 \exp(-bR^d)$ with the parameters $S_0 = 0.322\ 12, 0.108\ 45, 0.904\ 05$; $b = 0.696\ 83, 0.295\ 79, 1.548\ 32$; $d = 1.611\ 16, 1.917\ 06, 1.009\ 52$ for s, σ and π bonds, respectively. The values of the model parameters $G_s = 1$, $G_\sigma = 5$, $G_\pi = 1.5$ were obtained from a comparison

Table 3. Parameters of the nuclear spin Hamiltonian of ¹⁴¹Pr in LaF₃ and PrF₃.

Y C ₂	LaF ₃ :Pr		PrF ₃		
	GS ³ H ₄ [13]	³ P ₀ [32]	GS ³ H ₄ [14]	GS ³ H ₄	³ P ₀
1	2	3	4	5	6
γ_{XX}/γ	3.83	1	2.55	2.59	0.97
γ_{YY}/γ	1.95	1	2.49	3.01	0.97
γ_{ZZ}/γ	7.82	1	7.72	7.07	0.97
D (kHz)	4185	293	4310	-3556	+340
E (kHz)	146	50	300	+517	+100

Neglecting the core polarization terms, we can write the Hamiltonian of the magnetic hyperfine interaction in the form $H_{\text{hf}} = \tilde{\mathbf{A}}\tilde{\mathbf{I}}$, where [29]

$$\tilde{\mathbf{A}} = \frac{2}{15}\mu_{\text{B}}\gamma\hbar\langle r^{-3} \rangle \sum_i [15\vec{\mathbf{l}}_i + 8\vec{\mathbf{s}}_i - \vec{\mathbf{l}}_i(\vec{\mathbf{l}}_i\vec{\mathbf{s}}_i) - (\vec{\mathbf{l}}_i\vec{\mathbf{s}}_i)\vec{\mathbf{l}}_i] \quad (12)$$

the sum is taken over 4f electrons, $\gamma(^{141}\text{Pr}) = 1.31 \text{ kHz G}^{-1}$ is the nuclear gyromagnetic ratio, and $\langle r^{-3} \rangle = 4.054 \text{ a.u.}$ This value of $\langle r^{-3} \rangle$ is to be used when working in the total space of states of the 4f² configuration to obtain the experimental value of the effective hyperfine constant $A_J(^3\text{H}_4) = 1093.8 \text{ MHz}$ [29, 30]. Assuming the sum of the electronic Zeeman energy H_Z and the hyperfine interaction H_{hf} as a perturbation, we obtain within the second order of the perturbation theory [31] the following parameters of the nuclear Hamiltonian, related to the electronic state $|k\rangle$ of an ion:

$$\gamma_{\alpha\beta}^{(k)} = \gamma \left[\delta_{\alpha\beta} + \sum_n \frac{\langle k|A_\alpha|n\rangle\langle n|\mu_\beta|n\rangle + \langle k|\mu_\beta|n\rangle\langle n|A_\alpha|n\rangle}{\gamma\hbar(E_k - E_n)} \right]. \quad (13)$$

The tensor $\tilde{\mathbf{P}}$ contains three contributions corresponding to the magnetic hyperfine interaction in second order (the pseudoquadrupole interaction), the average value of the quadrupole hyperfine interaction H_Q , and the gradient of the lattice electric field. In particular,

$$P_{zz}^{(k)} = \sum_n (E_k - E_n)^{-1} [|\langle k|A_z|n\rangle|^2 - (|\langle k|A_x|n\rangle|^2 + |\langle k|A_y|n\rangle|^2)/2] + \langle k|B_{zz}^Q|k\rangle + P_{zz}^{\text{lat}}. \quad (14)$$

Here

$$B_{zz}^Q = -\frac{e^2Q\langle r^{-3} \rangle}{30I(2I-1)} \sum_i [3l_{iz}^2 - l(l+1)], \quad (15)$$

$$P_{zz}^{\text{lat}} = \frac{3e^2Q(1-\gamma_\infty)}{4I(2I-1)} \sum_L q_L \frac{3\cos^2\vartheta_L - 1}{R_L^3}, \quad (16)$$

$Q = -5.9 \times 10^{-12} \text{ nm}^2$ is the quadrupole moment of ¹⁴¹Pr, $\gamma_\infty = -80$ is the antishielding constant and $R = -0.2$ is the Sternheimer shielding constant [30]. In table 3 the calculated principal values of the nuclear g -tensor and the quadrupole constants D and E in the ground state (GS) and in the excited state ³P₀ of Pr³⁺ are compared with the experimental data. The tensors $\tilde{\gamma}$ and $\tilde{\mathbf{P}}$ have one of their principal axes (Y) along the symmetry axis C₂. According to results of the calculations, in the ground state the principal axis X of the $\tilde{\gamma}$ tensor is declined from the c -axis by 9.8°, and for the $\tilde{\mathbf{P}}$ tensor this angle equals 5°. These angles are close to the angle 8.6° determined from the experimental data [13] which defines the direction of the

common principal axis X of $\tilde{\gamma}$ and \tilde{P} tensors in LaF₃:Pr. If the principal axes coincide, the nuclear Hamiltonian (11) takes the form

$$H_I = -\hbar \sum_{\alpha} \gamma_{\alpha\alpha} I_{\alpha} H_{0\alpha} + D[I_Z^2 - I(I+1)/3] + E(I_X^2 + I_Y^2). \quad (17)$$

Parameters of this Hamiltonian determined in [13, 14, 32] are given in table 3. As is seen, the results of our calculations based on the set of the crystal field parameters which has been obtained in this study are in qualitative agreement with the experimental data. The lattice contribution P_{zz}^{lat} dominates in the excited state 3P_0 , and the principal axis Z of the electric field gradient is declined from the C_3 axis by 9° . For the first time the large anisotropy of the measured enhanced nuclear g -tensor in the ground state has been given an explanation on the microscopic level. The calculated D and E values in the ground state differ remarkably from the measured ones. Some possible reasons for errors in the calculations are evident (neglecting of the core polarization and the overestimated shielding of the 4f-electron electric field at the nucleus, in particular); however, more experimental data are necessary for improvement of the theoretical analysis.

5. Conclusion

The longitudinal and transversal components of the magnetic susceptibility tensor in PrF₃ were measured in the temperatures range 2–300 K. Because all electronic crystal field states of Pr³⁺ ions in the low-symmetry (C_2) crystal field are singlets, and the gap between the ground state and the first excited sublevel of the lowest multiplet 3H_4 is more than 70 K [7, 8], one may expect constant values of the susceptibilities at temperatures below 10 K. However, a remarkable increase of both the longitudinal and transversal susceptibilities with decreasing temperature below 20 K was observed, which we ascribe to Pr³⁺ ions affected by intrinsic lattice defects. A crystal field analysis based on the magnetic susceptibility data and calculations in the framework of the exchange charge model was carried out. The set of crystal field parameters related to the crystallographic system of coordinates has been obtained and used to reproduce successfully the crystal field energies known from the literature, the monotonic decrease of the longitudinal susceptibility with increasing temperature, and the broad maximum of the transversal susceptibility at 60 K. The calculated parameters of the effective spin Hamiltonian of the ¹⁴¹Pr nuclei in PrF₃ agree satisfactorily with experimental data obtained earlier from NMR measurements [13, 14, 31].

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