

Low temperature magnetic properties of rare-earth trifluorides

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The magnetic susceptibility of PrF_3 Van Vleck paramagnet was measured in the external magnetic fields directed across and along the crystallographic c -axis at temperatures 2-300 K. The 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 and field 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. Also PrF_3 was studied as a promising material for nuclear magnetic polarization of liquid 3He . An affirmative conclusion about possibility of the direct magnetic coupling between two nuclear systems of 3He and ^{141}Pr through a surface of PrF_3 was drawn. This conclusion is a result of PrF_3 powder study by magnetometry, optical microscopy and theoretical calculations. The direct magnetic coupling was observed by NMR of 3He and ^{141}Pr in nonoriented powder of PrF_3 at temperature of 1.6 K and NMR frequency $f_{NMR} = 6.63$ MHz. Thus, PrF_3 has been proposed as a material for the dynamic polarization of 3He nuclei.

The magnetic susceptibility of CeF_3 paramagnet was measured in the external magnetic fields directed across and along the crystallographic c -axis at temperatures 2-300 K. The crystal field analysis was carried out. The crystal field energies of Ce^{3+} ions were calculated in rather good agreement with the experimental data. Result of our theoretical calculation of magnetic susceptibility in CeF_3 single crystal also was found in a good agreement with the experimental data. This calculation based on the crystal field theory explains the anomalous temperature behavior of the CeF_3 magnetic susceptibility.

Low temperature magnetic properties of PrF_3 Van Vleck paramagnet were studied by magnetometry. Set of the crystal field parameters for the Pr^{3+} ions in the framework of the semi-phenomenological exchange charge model has been calculated (Table 1). Both the energies of ground state multiplet 3H_4 and energies of the excited multiplets 3H_5 , 3F_2 , 3F_3 , 3F_4 , 1D_2 are obtained rather satisfactory by use this parameter set.

Table 1. The crystal field parameters calculated in the framework of the exchange charge model for Pr³⁺ ion hosted in PrF₃ matrix.

B _{kq} (cm ⁻¹)	B ₂₀	B ₂₂	B ₄₀	B ₄₂	B ₄₄	B ₆₀	B ₆₂	B ₆₄	B ₆₆
<i>Re</i>	-167.5	-40.3	637.5	428	489	612	-1006	-155	-533
<i>Im</i>		-12.5		135	259		70	-452	-652

The temperature and field dependences of the principal values of the magnetic susceptibility tensor in Van Vleck paramagnet PrF₃ have been studied from direct measurements with the SQUID magnetometer. The temperature and field dependencies of magnetic susceptibilities have been calculated using the obtained set of the crystal field parameters. Also, the agreement between the calculated and previously measured parameters of the effective nuclear spin Hamiltonian of the ¹⁴¹Pr nuclei in PrF₃ is rather satisfactory. These facts confirm physical meaning of the crystal field parameters obtained in this work.

The PrF₃ Van Vleck paramagnet was studied as a promising material for the nuclear dynamic polarization of ³He. The nuclear spins of Pr³⁺ Van Vleck ions of the crystal lattice are effectively coupled to the electron cloud by a hyperfine interaction. An external magnetic field **H** induces a magnetic moment of the electron cloud in the nonmagnetic ground state. However, it is necessary to put the electron shell in an excited state to transfer of polarization from the electron cloud to nuclear spins. During relaxation from this excited state, part of the electron polarization will be transferred to the nuclear spin system through a hyperfine interaction. The application of high magnetic fields allows making the energy distance between the ground level and the excited level equal to some laser output line. Also, high magnetic fields have accordingly to be applied in order to reduce the loss of the ¹⁴¹Pr polarization which results from the relaxation mechanism by the paramagnetic impurity.

Using the obtained set of the crystal field parameters the field dependence of the Stark energy levels of Pr³⁺ ions in PrF₃ lattice matrix have been simulated for all orientations of the crystal in applied magnetic field up to

40 T. In spite of so high applied magnetic field the energy distance between ground state and lowest excited state of ${}^3\text{H}_4$ multiplet was found rather invariable. This phenomenon presents some difficulties to excite the electron shell of Pr^{3+} ions. Our simulation seems rather realistic because the calculation method gives an adequate description of the PrF_3 magnetic susceptibility at applied fields up to 55 kOe at least.

The polarization transfer in the surface of solid PrF_3 between nuclear systems of ${}^{141}\text{Pr}$ and ${}^3\text{He}$ can be achieved if the transition frequencies of these sorts of nuclei coincide with each other at certain external magnetic field. The ${}^{141}\text{Pr}$ nuclear transition frequencies were calculated for applied magnetic field of the value up to 40 kOe. Then these field dependencies for ${}^{141}\text{Pr}$ nuclei were compared with the dependence of nuclear transition frequency on magnetic field for ${}^3\text{He}$ nuclei. We concluded that PrF_3 single crystal should be oriented at external field so that $\mathbf{H} \parallel ac$, where ac is the cleavage plane of PrF_3 .

Important aspect to make possible the polarization transfer to ${}^3\text{He}$ nuclear system is the absence of the defect paramagnetic centers on the surface of PrF_3 because they prevent the direct magnetic coupling between two nuclear systems of ${}^{141}\text{Pr}$ and ${}^3\text{He}$. Our investigations by optical microscopy have shown rather perfect surface of the PrF_3 crystal powder particles suggesting that the surface is not abundant of the defect paramagnetic centers. The investigations of fine-dispersed PrF_3 powders by magnetometry have not revealed large amount of the paramagnetic centers on the surface. Moreover, we have experimentally observed the resonant magnetic coupling between nuclear systems of ${}^{141}\text{Pr}$ and ${}^3\text{He}$ studying the NMR in nonoriented powder of PrF_3 put into liquid ${}^3\text{He}$. This effect was observed at NMR frequency of 6.63 MHz and temperature of 1.6 K.

The crystal field analysis in CeF_3 in the framework of crystal field theory has been carried out. The crystal field energies of Ce^{3+} ions were calculated in rather good agreement with the experimental data. Low temperature magnetic properties of CeF_3 have been studied by the SQUID magnetometry. The

temperature dependencies of the susceptibility in a single crystal have been measured and calculated for orientation of the crystal $H||c$ and $H\perp c$ at external magnetic field. The theoretical calculation of magnetic susceptibility in CeF_3 has been found in a good agreement with the experimental data. This susceptibility analysis based on the crystal field theory explains the anomalous temperature behavior of the magnetic susceptibility at temperatures $T < 50$ K and $T > 50$ K.

学位論文審査結果の要旨

Savinkov Andrey Vladimirovich 君の学位論文について、上記5名の審査委員による査読の後、平成19年8月3日に口頭発表が行われた。同日に審査会を開き、以下のように博士(学術)に値するものと判定した。

本論文はあまり研究が進んでいない RF_3 系磁性体の研究を行った。希土類の Pr は Van-Vleck 常磁性を示し 0.1mK 程度の超低温で核磁気転移する可能性があるが、その研究には Pr イオンのエネルギー準位を正確に評価することが必要である。多くの結晶場パラメーターを高精度で計算し、自らの実験で得られた磁化をよく説明した。また、この方法を CeF_3 にも適用し、50K 以下の特異な磁化の変化を高精度で解析した。

肺の NMR トポグラフィーに利用される高偏極の 3He を得る新しい方法として考えられているダイナミカルな核偏極法に PrF_3 を使用する可能性を研究した。 ^{141}Pr は 3He と近い NMR 共鳴周波数を持つ磁場があることが計算から予想され、共鳴的な磁気結合により偏極移動が起こる。また、結晶表面の Pr イオンが常磁性中心として作用し、この偏極移動を伝える。Savinkov 君は粉末状の PrF_3 試料を準備し、磁化測定によりこの物質ではあまり多くの常磁性中心が発生していないことを明らかにした。次に、粉末 PrF_3 と液体 3He に浸した粉末 PrF_3 の NMR 測定を行い、Pr 核と 3He 核の間に共鳴的な磁気結合の存在を明らかにした。以上のことから本論文は博士の学位に値するものと判断した。