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Crystal field in praseodymium gallium garnet

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Abstract

To study the crystal field (CF) at praseodymium sites in praseodymium gallium garnet (PrGG) we investigated experimentally and theoretically its Raman scattering, magnetization, and far infrared magnetotransmission. The experimental data can be described by a set of CF parameters which are rather close to those available for analogous neodymium-doped rare earth gallium garnets. © 1998 Elsevier Science S.A.

Keywords: Rare earth garnets; Crystal field effects; Raman scattering; Magnetization curves; Far infrared absorption

1. Introduction

Recent detailed analysis of the optical absorption, the site selective excitation, and the luminescence spectra of the Pr^{3+} in $RE_3Ga_5O_{12}$ (REGG, RE=Y, Gd, Pr) indicates that the values of the crystal field (CF) parameters at praseodymium sites differ from the general trend in the RE^{3+}: REGG series [1]. This difference, more pronounced in $Pr_3Ga_5O_{12}$, has been discussed in terms of a possible structural anomaly, an inadequacy of the theoretical framework used to extract the CF parameters from the data, and the incomplete set of the experimentally determined CF levels [1].

Pursuing the study of the CF in PrGG, in this work we investigate experimentally and theoretically various properties including the Raman scattering, the magnetization, and the far infrared magnetotransmission. The experimental data, carrying information about the CF states of the lowest-energy $^3H_4$ multiplet, are used to deduce a new set of phenomenological CF parameters for the compound studied. An elucidation of the CF interaction at Pr sites in PrGG is also important for Pr-containing cuprates in which the CF-split ground quasitriplet state, similar to that in garnets [2], is believed to play a significant role in the suppression of superconductivity [3].

2. Experiment

Single crystals of PrGG were grown by the flux method described elsewhere [4]. The magnetization measurements in applied fields up to 14 T have been performed on two spherical single crystals with diameters of 3.15 mm and 1.05 mm using a standard extraction method.

Raman spectra have been measured in right-angle scattering geometry on an oriented and carefully polished parallelepiped $2.9\times2.5\times1.2$ mm^3 with edges oriented along the z, x' and y' direction, respectively [4]. The common notation $z\equiv[001]$, $x'\equiv[110]$, $y'\equiv[1\text{–}10]$ is used. The sample was mounted in a continuous-flow liquid-He optical cryostat. The measurements were performed at 40 K, 100 K and at room temperature using the 488, 496.5, 501.8 and 514.5 nm lines of an Ar^+ laser for excitation. The scattered light was analysed using a PC-controlled SPEX-14018 double spectrometer equipped with standard photon-counting detection.

The low-temperature far infrared transmission data on the PrGG platelets have been obtained using the laser based spectrophotometer FIRM [5] with the 17.2 and 19.5 cm^{-1} laser lines. A silicon bolometer served to record the radiation transmitted through the sample placed in a 8 T

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superconducting solenoid as a function of the sweeping magnetic field parallel to the [111] direction.

3. Results and discussion

The experimental magnetization curves at 1.5 K for magnetic fields up to 14 T applied along the [100], [110] and [111] directions are plotted in Fig. 1. In magnetic fields above ~3 T the magnetization is anisotropic with [111] being the magnetic easy axis. The extraction method was also used to measure the magnetic susceptibility at temperatures up to 300 K. The susceptibility was found to be isotropic and identical with that reported earlier [4] within the experimental error.

The Raman spectra measured in *zz*, *x′y′*, and *zy′* configurations with the 514.5 nm excitation at 40 K and 100 K are shown in Figs. 2 and 3, respectively. We note that the spectra in these figures were obtained in different runs. Applying the selection rules [6], we were able to identify in our spectra the 25 Raman-active ($3A_{1g}+8E_g+14T_{2g}$) phonons except one with the T_{2g} symmetry. The features at 16.6 and 64.2 cm^{-1} are electronic transitions from the ground state to the first and second excited CF levels of the $^3H_4$ multiplet of the Pr^{3+}, the peak at 47.6 cm^{-1} corresponds to a transition from the first to the second excited level. This conclusion is supported by the data available for other RE garnets indicating that no phonon mode is expected to lie below the lowest T_{2g} phonon observed at 107 cm^{-1} in our case. Additional support comes from a comparison with the PrGG optical data [1] as well as from Raman intensity calculations discussed below.

We found that the above mentioned magnetization cannot be explained in terms of the available CF parameters [1]. In particular, the calculation based on the latter parameters leads to the magnetic easy axis parallel to [100]

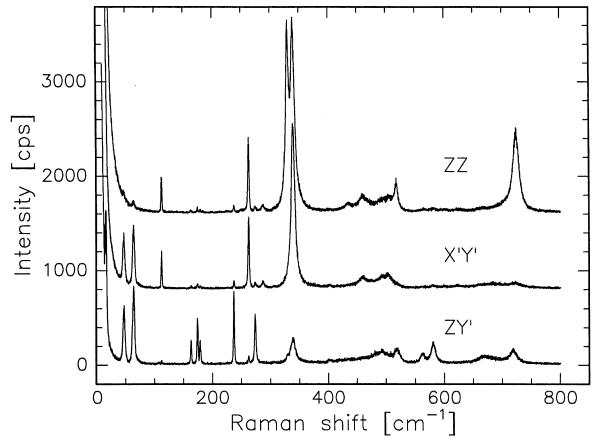

Fig. 2. Raman spectra of PrGG at ~40 K in *zz*, *x′y′*, and *zy′* scattering configurations for the laser excitation wavelengths of 514.5 nm. The vertical axis is for the *zy′* curve; for clarity, the *x′y′* and *zy′* curves are shifted upwards by 800 and 1600 cps, respectively.

which contradicts our data in Fig. 1. We have thus deduced a new set of phenomenological CF parameters in PrGG by a least-squares fit to data mainly associated with the CF states of the lowest *J* multiplet. These data include the 1.5 K magnetization data up to 14 T (Fig. 1), the susceptibility data from 4.2 to 300 K [4], the CF levels at 16.6 and 64.2 cm^{-1} revealed by our Raman measurements and the available levels at 517 and 706 cm^{-1} [1]. The CF and Zeeman hamiltonians have been diagonalized within the 63 states of the seven lowest *J* multiplets. Small differences between the free-ion wave functions and energies we used [7] and those in [1] are negligible for the purpose of the present study. Our best-fit CF parameters, together with those available for PrGG [1] and Nd-doped GdGG [8], are given in Table 1. Our calculated $^3H_4$ CF levels are the following: -4 (Γ_4), 18 (Γ_1), 66 (Γ_2), 462 (Γ_4), 466 (Γ_1), 479 (Γ_2), 517 (Γ_3), 644 (Γ_3), and 706 (Γ_1) cm^{-1}. It should be noted that the energies and in particular the symmetries of the three lowest CF states, governing the anisotropy of

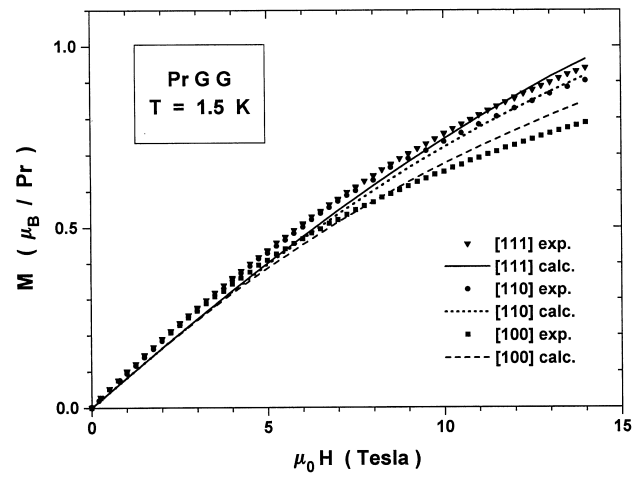

Fig. 1. Experimental and theoretical magnetization curves of PrGG at 1.5 K for the magnetic field applied along the [100], [110], and [111] directions.

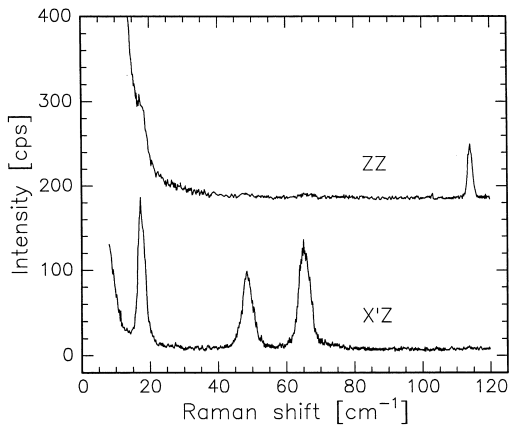

Fig. 3. Details of the low-frequency part of the *zz* and *x′z* spectrum at ~100 K for the laser excitation wavelength of 514.5 nm. The vertical axis is for the *x′z* curve; the *zz* curve is shifted upwards by 180 cps.

Table 1
CF parameters (in cm^{-1}) of Pr^{3+} in PrGG obtained in this work and in Ref. [1] (rotated to more common local symmetry axes [11]) as well as those for Nd^{3+} in GdGG.

Parameters	Pr^{3+} (this work)	Pr^{3+} [1]	Nd^{3+} [8]
B_{20}	−334	−384	−193
B_{22}	144	50	156
B_{40}	−2630	−3059	−2543
B_{42}	252	361	220
B_{44}	1126	1196	1126
B_{60}	932	605	914
B_{62}	−207	−606	−225
B_{64}	1622	1280	1499
B_{66}	−199	−292	−139

magnetization, obtained in [1] are different: −1 (Γ_1), 13 (Γ_2), and 55 (Γ_4).

The magnetization curves calculated from our best-fit CF parameters and taking into account the existence of magnetically unequivalent Pr sites are seen in Fig. 1. They agree with the experimental data reasonably well. Also the calculated susceptibility compares well with the above mentioned experimental data. It is almost perfectly isotropic and agrees within <4% with the available data [4].

Using the latter parameters we have applied the standard Judd-Ofelt theory to calculate the relative intensities of the electronic Raman transitions within the $^3H_4$ multiplet. Considering the formulae given in [9], available data for the radial matrix elements $<4f|r^2|4f>$ and $<4f|r|5d>^2$, and the energies of the excited configurations $h\omega_{5g}$ and $h\omega_{5d}$ (see, e.g., [10]), as well as the specific temperature of the experiment, we arrived at results which can be summarized as follows. In agreement with the experimental data (Fig. 3), the theoretical intensities of the Raman active transitions within the ground state CF quasitriplet in the *zz* configuration are negligible in comparison with those in the $x'y'$ and zy' configurations which are mutually comparable. The Raman transitions from the ground state quasitriplet to the higher energy $^3H_4$ CF states are in general weaker by a factor of 3 or more in comparison with the strong transitions within the quasitriplet. The feature observed at ~519 cm^{-1} in the zy' configuration (Fig. 2) and absent in the $x'y'$ configuration was found to agree very well with the prediction of the theory and thus is ascribed to a CF transition. In the *zz* configuration, the sharp feature at this frequency is identified with an A_{1g} phonon, also observed in spectra of other REGG (see, e.g. [6]).

A Zeeman study is known to provide a good test for the reliability of CF parameters. The positions of the transmission minima, predicted considering our CF parameters and shifting the calculated first excited level to coincide with its above mentioned Raman value of 16.6 cm^{-1} at $H^a=0$ T, agree rather well with the experimental data (Fig. 4). We note that the theoretical minima at 4.1 T (17.2 cm^{-1} line) and 7.4 T (19.5 cm^{-1}), and at 5.7 T (17.2 cm^{-1}) and

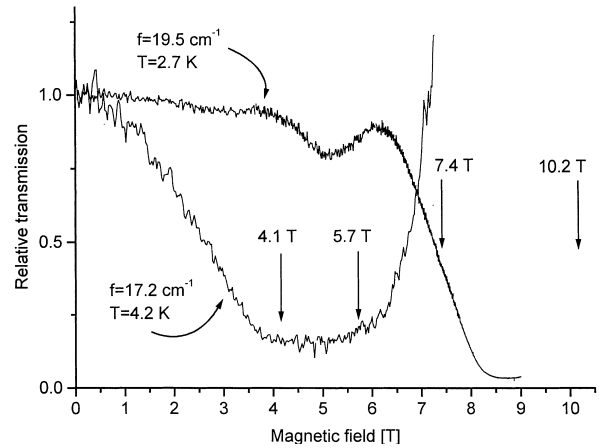

Fig. 4. Transmission spectra of PrGG for the photon frequency of 17.2 and 19.5 cm^{-1} measured at 4.2 and 2.7 K, respectively. The magnetic field is applied along the [111] axis. The arrows show positions of the theoretically predicted transmission minima.

10.2 T (19.5 cm^{-1}) correspond to unequivalent sites characterized by the directional cosines $[1/\sqrt{3}, 0, \sqrt{(2/3)}]$ and $[1/\sqrt{3}, \sqrt{(2/3)}, 0]$, respectively. The shallow minimum observed on the 19.5 cm^{-1} laser line at ~5.5 T, not explained by our theory, is tentatively ascribed to sample misorientation.

In summary, analyzing the data obtained by several different experimental methods, we arrived at a set of phenomenological CF parameters for the Pr^{3+} ions in PrGG. These parameters are close to those in Nd^{3+}: GdGG.

Acknowledgements

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