

## Comment on "Spectra and energy levels of $\text{Er}^{3+}$ ( $4f^{11}$ ) in $\text{NaBi}(\text{WO}_4)_2$ "

### [J. Appl. Phys. 94, 7128 (2003)]

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A recent article by Gruber *et al.* [Gruber, J. Appl. Phys. **94**, 7128 (2003)] reports the measurements of the optical absorption and photoluminescence spectra of  $\text{Er}^{3+}$  in  $\text{NaBi}(\text{WO}_4)_2$  (NBW) and the results of the interpretation and fitting of the observed crystal-field (CF) splitting of  $\text{Er}^{3+}$  multiplets with a quasicenter model. In the light of available, previously published information, we argued that these conclusions are not warranted. As a proof, the composition of the  $\text{Er}^{3+}$ -NBW wave functions and the energy levels derived from the final obtained CF parameters have been checked through the simulation of the temperature-dependent paramagnetic susceptibility  $\chi_m$  according to the Van Vleck formalism and, unfortunately, experimental curves of  $\chi_m$  versus  $T$ , measured in parallel and perpendicular directions to the  $c$  axis of the NBW crystal, were not adequately reproduced. The same simulation was carried out with a set of free ions and CF parameters resulting from our previous polarized CF analysis of  $\text{Er}^{3+}$  in a NBW crystal, and the agreement with the measured  $\chi_m$  versus  $T$  curves is a clear indication of the validity and physical meaning of our earlier performed CF analysis. © 2004 American Institute of Physics. [DOI: 10.1063/1.1792382]

A recent article by Gruber *et al.*<sup>1</sup> reports the measurements of the optical absorption (OA) and photoluminescence (PL) spectra of  $\text{Er}^{3+}$  in  $\text{NaBi}(\text{WO}_4)_2$  (NBW), and the results of the interpretation and fitting of the observed crystal-field (CF) splitting of  $\text{Er}^{3+}$  multiplets with a quasicenter model.

Contrary to the belief of these authors, after the paper of Kaminskii *et al.*,<sup>2</sup> a continuous effort has been undertaken to study the properties of NBW single crystals. This effort included aspects related to the synthesis and crystal-growth procedures;<sup>3-6</sup> the structural characterization,<sup>7</sup> which corrects previous<sup>2,8</sup> space-group assignments; the anisotropic linear optical properties such as refractive indices,<sup>4,9</sup> infrared absorption and Raman spectra,<sup>10,11</sup> and scintillating capability;<sup>12-14</sup> the nonlinear optical properties such as Raman shifting<sup>15</sup> and up conversion;<sup>16</sup> and finally, the detailed spectroscopy and CF analyses of several rare-earth  $\text{R}^{3+}$  impurities, namely,  $\text{Er}^{3+}$ ,<sup>17,18</sup>  $\text{Pr}^{3+}$ ,<sup>19</sup>  $\text{Nd}^{3+}$ ,<sup>20,21</sup> and  $\text{Yb}^{3+}$ ,<sup>18</sup> in NBW crystals.

From the published information, the following are now well established:

(a) The tetragonal structure of NBW belongs to the non-centrosymmetric space group  $\bar{I}4$  (No. 82),  $Z=2$ , with the  $\text{Na}^+$  and  $\text{Bi}^{3+}$  cations sharing two nonequivalent crystal sites,  $2b$  and  $2d$ , both with an  $S_4$  point symmetry. One of these sites is preferentially occupied by  $\text{Bi}^{3+}$ , whereas the other contains a larger amount of  $\text{Na}^+$  cations. Although in both sites  $\text{Bi}^{3+}$  has an eightfold oxygen coordination, the Bi-O distances and O-Bi-O angles differ for these two sites. Since  $\text{R}^{3+}$  ions replace

$\text{Bi}^{3+}$ , at least two different phenomena contribute to the large observed bandwidth of the  $\text{R}^{3+}$  optical spectra: (i) the overlapping  $\text{R}^{3+}$  contributions arising from these two sites and (ii) the broadening associated to the centers resulting from different short-range  $\text{Na}^+$  and  $\text{Bi}^{3+}$  distributions around each one of the two  $\text{R}^{3+}$  sites mentioned previously.

- (b) The presence of optical transitions associated to the polarization in the  $\text{R}^{3+}$  optical spectra in NBW has been well documented for a number of ions. Figure 1 includes some selected examples for  $\text{Er}^{3+}$ ,  $\text{Nd}^{3+}$ , and  $\text{Pr}^{3+}$ . The  $S_4$  characteristics in the  $\sigma$ - and  $\pi$ -polarized spectra of  $\text{Er}^{3+}$  in NBW are by no means *weak* but are strongly exhibited [see for instance the 10 K polarized OA spectrum corresponding to the  $^4I_{15/2} \rightarrow ^4S_{3/2}$  transitions as it appears in Fig. 1(a)], and this situation is extensive to other  $\text{Er}^{3+}$  transitions as shown in Fig. 3 of Ref. 17. This is a major point of the current comment because it is only from polarized low-temperature measurements of the optical spectra, through the attribution of the corresponding irreducible representations to the energy levels, which will be possible to correctly ascertain the splitting of  $^4S_{3/2}$  for  $\text{Er}^{3+}$  in NBW. The erroneous determination of the low-lying  $^4S_{3/2}$  energy level in Ref. 1 leads to a poor description of the  $^4I_{15/2}$  ground state of  $\text{Er}^{3+}$  in NBW displayed in Fig. 4 and therefore to a systematic uncertainty on the hot bands described.
- (c) A set of CF parameters derived from the phenomenological analysis of the optical spectra of  $\text{Nd}^{3+}$  in NBW (and obviously its comparison with the results from more or less empirical models) *does not constitute* an adequate starting set for analyzing the CF splitting of  $\text{Er}^{3+}$  in the same host. The explanation is related to the

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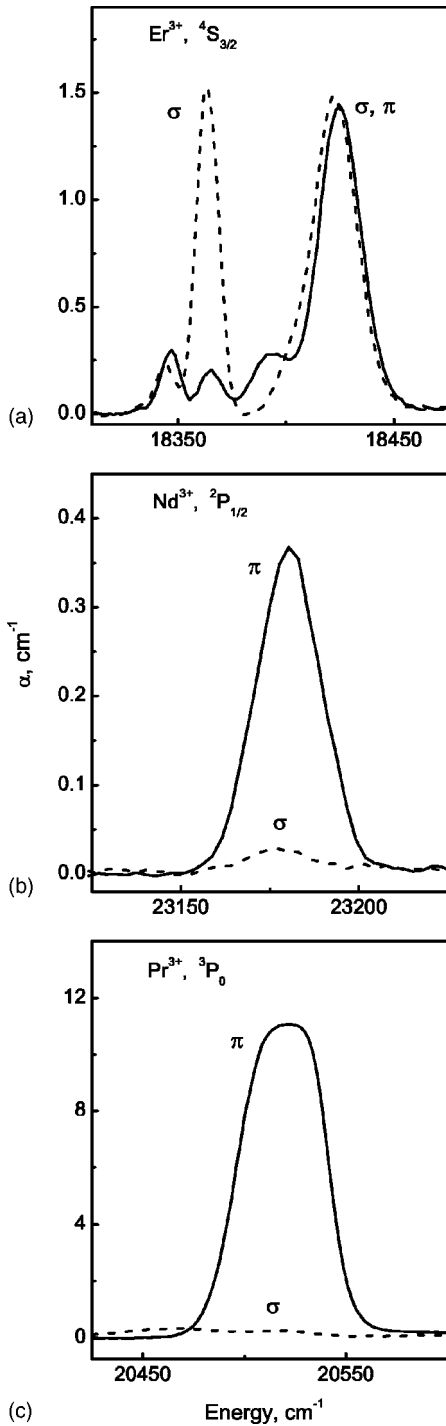


FIG. 1. Polarized 10 K optical absorption coefficient  $\alpha$  of  $R^{3+}$ -doped NBW single crystal. Continuous lines:  $\pi$  spectra. Dashed lines:  $\alpha$  spectra. (a)  $Er^{3+}$ ,  $[Er]=0.92 \times 10^{20} \text{ cm}^{-3}$ ; (b)  $Nd^{3+}$ ,  $[Nd]=0.3 \times 10^{20} \text{ cm}^{-3}$ ; and (c)  $Pr^{3+}$ ,  $[Pr]=0.5 \times 10^{20} \text{ cm}^{-3}$ .

changes and distortions in the local symmetry created in the crystal when  $Bi^{3+}$  ions are substituted by larger  $Nd^{3+}$  (or  $Pr^{3+}$ ) cations, which became evident in the polarized low-temperature OA and PL spectra for these cations in NBW. The optical spectra display features inconsistent with the  $S_4$  selection rules for the induced electric dipole and magnetic dipole transitions and are better described assuming an average  $C_2$  site symmetry and the corresponding 14 CF parameters defining this

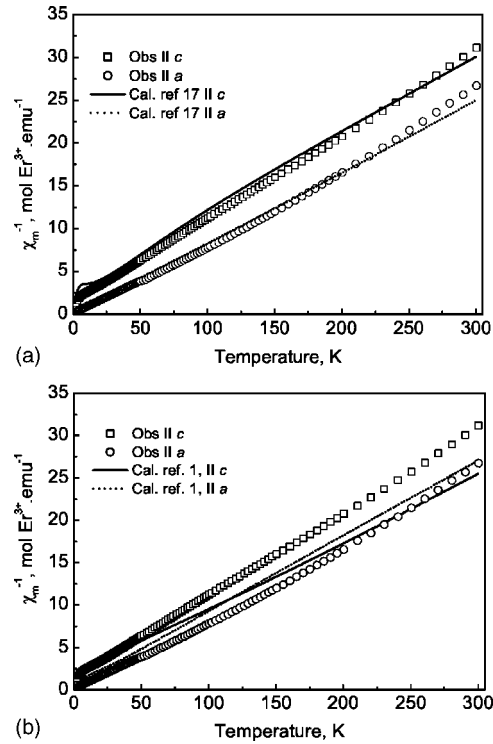


FIG. 2. Comparison between the observed and simulated reciprocal paramagnetic susceptibility versus  $T$  curves for  $Er^{3+}$  in  $NaBi(WO_4)_2$  (a) from free ion and CF parameters indicated in Ref. 17 and (b) from free ion and CF parameters in Ref. 1.

potential.<sup>19,20</sup> However, when  $Er^{3+}$  cations are embedded in NBW, a well-defined  $S_4$  behavior is observed in both the  $\sigma$ - and  $\pi$ -polarized spectra.<sup>17</sup> Additionally, the number of  $Nd^{3+}$  energy levels derived at 77 K in Ref. 2 is very limited, and discrepancies can be found with the more complete set of levels determined recently at 10 K.<sup>20</sup>

On the other hand, it is well known that the determination of a consistent set of CF parameters and associated wave functions for the energy levels of a given  $4f^N$  configuration allows the simulation of the thermal dependence of the paramagnetic molar susceptibility  $\chi_m$  for each direction of the  $R^{3+}$  point crystal site.<sup>22</sup>

The experimental curves of  $\chi_m$  versus  $T$  measured in parallel  $\parallel$  and perpendicular  $\perp$  directions to the  $c$ -crystal axis, i.e.,  $\parallel$  and  $\perp$  to the average fourfold-point symmetry axis of  $Er^{3+}$  in NBW ( $[Er]=0.92 \times 10^{20} \text{ cm}^{-3}$ ), are plotted in Fig. 2. Figure 2(a) shows the comparison with the corresponding  $\chi_m$  versus  $T$  curves calculated using the determined set of free ions and the  $S_4$  CF parameters for the  $Er$ -doped NBW crystal studied in Ref. 17. The same calculation has been also performed using the wave functions derived from the free ion<sup>23</sup> and the final CF parameters achieved in Ref. 1, and these latter  $\chi_m^{-1}$  versus  $T$  curves are included in Fig. 2(b). The good reproduction of the experimentally observed curves shown in Fig. 2(a) constitutes a successful test of the validity and physical meaning of our earlier CF analysis<sup>17</sup> and a proof of the accuracy of the determined wave functions for  $Er^{3+}$  energy levels in the NBW host.

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