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COMMENT

Comment on 'Unified explanation for optical and electron paramagnetic resonance spectra of Cr^{3+} ions in $LiNbO_3$ crystals' by M G Zhao and Y Lei

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Abstract. The named paper attempts to reproduce the optical and EPR spectra of Cr^{3+} centres in $LiNbO_3$ using *ab initio* calculations. This comment points out that the data the authors claim fit their calculations are incorrect. The method of calculation is brought into further question by its unusual predictions for sites that the named authors suggest are unoccupied but which have experimentally been shown to be both occupied and spectroscopically unremarkable.

The recent theoretical paper on the optical and electron paramagnetic resonance (EPR) spectroscopy of Cr^{3+} ions in $LiNbO_3$ by Zhao and Lei [1] is seriously flawed in a number of ways. Though their paper attempts to reproduce optical spectra using *ab initio* calculations, the experimental data that the authors claim their results fit well [2, 3] have been discredited [4]. Careful inspection of the optical absorption and fluorescence spectra of $Cr^{3+}:LiNbO_3$ show four sets of R-line pairs. One of these pairs does not fluoresce via the $^2E \rightarrow {}^4A_2$ transition, characteristic of R lines, because Cr^{3+} impurities responsible for these absorption features have a $^4T_2$ state energy that is depressed below the ^2E energy. Ions in these sites therefore decay via the $^4T_2 \rightarrow {}^4A_2$ transition, characterized by broad-band fluorescence. It is this site that is most strongly populated, and its absorption and fluorescence dominates optical spectra. This centre must, of course, also dominate EPR spectra. This centre was first reported and assigned nearly thirty years ago by Glass [5]. The principal experimental references of Zhao and Lei falsely assign these R lines as being hot-phonon side-bands [2] or to states that somehow absorb and fluoresce at different wavelengths despite being zero-phonon lines [3]. These mistakes have been rectified using simple site-selective fluorescence experiments [4]. This study revealed four secondary sites for Cr^{3+} in $LiNbO_3$, three of which have observable R lines. For Zhao and Lei to claim that they have provided a unified explanation for the spectroscopy of $Cr^{3+}:LiNbO_3$, they would have to start with correct experimental data that include the correct number of sites and accurate state energies. They have not done this.

The conclusions of Zhao and Lei were listed in three paragraphs that will be dealt with in turn.

(a) Their paper was not the first paper to attempt to unify the optical and EPR data for $Cr^{3+}:LiNbO_3$ as claimed. A paper in the same journal published some 18 months earlier had already accomplished this task by measuring ground-state splittings using fluorescence line

narrowing [4]. These data were directly compared to EPR studies [6, 7] so that the optical and EPR data could be tied together. Further comparison with ENDOR results [6] allowed definite site assignments to be made. The conclusions drawn have recently been confirmed by a further study of the influence on the optical spectra of the introduction of MgO to the melt [8]. Zhao and Lei state that they use only one adjustable model parameter, that is N, a covalency reduction factor, and that its value is justified by a further theoretical model published by Qiu [9]. It would appear, however, that their crystal relaxation parameters, f and ΔZ, are also free variables. The authors use different values when fitting the same centre to the two sets of experimental data [2, 3] though there is no mention of how these data are arrived at.

(b) In their discussion of the relaxation of Cr^{3+} ions in host crystals, Zhao and Lei appear to claim that their data for f and ΔZ are based on EPR results rather than *ab initio* calculations, though no justification for this is given. What is particularly puzzling is how values for f and ΔZ can be produced for the Li^+ site that the authors claim is unoccupied. If it is unoccupied then they cannot be measured. If they are based on a theoretical calculation then how is it done? The values used are unrealistically large, giving a shift along the C_3 axis of 0.2 and 0.3 Å respectively for the two centres. The calculations do not fit the data, so it is difficult to understand why such values have been chosen.

(c) Zhao and Lei compare their results with those of Qiu [9] and draw the conclusion that they are in some sense related. Qiu's calculations suggested that the energies of the ^2E states for the two different sites would vary by only 31 cm^{-1}, reasonable for a state that shifts in energy very weakly as a function of crystal-field strength, whereas Zhao and Lei calculate a difference of more than 1000 cm^{-1} between sites and a splitting between the ^2E states of one of the sites of 900 cm^{-1}. The latter values are so unreasonable that they do not prove the Li^+ site to be unoccupied, but rather suggest that there is a serious error in the calculations. Simple calculations (based on an earlier paper by Zhao and colleagues [10]) have previously been published that show that optical and ground-state spectra are mutually compatible [4].

A successful *ab initio* calculation requires five Cr^{3+} centres to be modelled. However, it also requires highly accurate information on the positioning of Cr^{3+} ions within the lattice. This information can only be obtained either from correct models of experimental data or direct techniques such as EXAFS. The work of Zhao and Lei uses neither of these, and their results are therefore highly dubious.

The most consistent assignment of the Cr^{3+} centre that dominates both optical and EPR spectra remains the Li^+ site, on the basis of ENDOR results [6], confirmed by EPR [7] and optical data [4, 8]. The paper that Zhao and Lei refer to with respect to ENDOR data [11] is a review of both intrinsic and extrinsic defects in $LiNbO_3$ that barely mentions Cr^{3+} impurities, and certainly does not provide independent evidence that the main centre is the Nb^{5+} site as they claim. The R lines discussed by Jia *et al* [2] are distortions of the main site [4]. The minority Nb^{5+} site is increasingly occupied for crystals more heavily doped with Mg^{2+} [4, 8], and distorted versions of this site also exist [4]. A final question to answer is that of why the Li^+ site has energy levels shifted to higher values despite the fact that the Nb^{5+} ion has a closer arrangement of Cr^{3+} ions. There are at least two possible answers to this question. One is that the actual substitutional positions of the Cr^{3+} ions and the relaxation positions of the O^{2-} ions may be quite different from those of the undoped crystal (as discussed but not convincingly calculated by Zhao and Lei). A second possibility is that there is a large difference between the covalencies of Nb–O and Li–O bonds [12] that can cause the electron–electron energies interaction of the Cr–O bonds to

vary considerably [13] between different lattice positions. The values of N, that represents covalency, taken by Zhao and Lei are very similar for the two sites, despite the fact that the Cr–O bonds will be influenced by the different combinations of Li–O and Nb–O bonds that surround the different substitutional centres.

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