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AN AB-INITIO CALCULATION FOR PRESSURE SHIFTS OF OPTICAL ABSORPTION BANDS IN Fe$^{2+}$-BEARING GARNETS

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Résumé. Nous avons réalisé un calcul "ab-initio" pour corrélérer les bandes d'absorption optique du Fe$^{2+}$ dans les grenats, avec leurs structures cristallines à l'aide de la théorie SCF des orbitales d proposée par Zhao et al. Connaissant les paramètres cristallins, on peut calculer les niveaux d'énergie de Fe$^{2+}$ dans le cristal. On montre que le changement de structure cristalline est prépondérant dans le déplacement des bandes sous l'action de la pression. Dans les grenats, le fer est en symétric dodécaédrale $D_2$, de nature fortement ionique comme le confirment les mesures d'effet Mössbauer.

Abstract. An ab-initio calculation has been made to investigate the relation between the optical absorption bands of Fe$^{2+}$ in garnet and its crystal structure, adopted the self-consistent-field(SCF) d-orbital theory proposed by Zhao et al. The energy levels of Fe$^{2+}$ in crystal can be got as long as we know the crystalline parameters. It is shown that the change of crystal structure plays the main role in the shifts of crystal bands and that Fe$^{2+}$ at dodechedral $D_2$ site in garnet is of highly ionic nature which is in accord with the isomer shifts and quadrupole splittings of Fe$^{2+}$ in garnet.

One area of solid state physics where high pressure studies have been important is that of d-d transitions of metal ions in crystals. Usually, pressure shifts of optical absorption bands provide a useful method for distinguishing and identifying specific transitions by comparison with theoretically predicted shifts. A difficulty in predicting high pressure effects, however, arises from the lack of the satisfactory theory which relates the d-d transitions of ions in crystals to the parameters of crystalline lattice since the pressure effects are usually a direct consequence of its crystal structure. Recently, an ab-initio calculation has been made for the spectra of Fe$^{2+}$, Mn$^{2+}$, Cr$^{3+}$, Co$^{2+}$, and Cu$^{2+}$ in crystals /1-5/ on the basis of approximation self-consistent-field(SCF) d-orbital theory which allows us to establish a relation between d-d transitions and its crystalline parameters. Therefore it is possible now to investigate more fully the pressure shifts with the crystalline parameters under various pressure.

Here the attention is focussed on the Fe$^{2+}$ in silicate garnets which are generally assumed to be important mantle silicate minerals. The uses of the superposition model and point-charge ionic bonding model to analyze the spectrum of Fe$^{2+}$ in pyrope garnet have been described /6/, adopted Zhao and Duls d-orbital for Fe$^{2+}$.

In this communication, we extend our earlier work and are concerned with theoretically predicted pressure shifts of optical absorption bands in Fe$^{2+}$-garnets.

I - THEORETICAL ANALYSIS

Garnet crystallines in the space group Ia3d. The Fe$^{2+}$ ions occupy the position 24c with dodechedral $D_2$ point symmetry. It is generally accepted that Fe$^{2+}$ is responsible for a group of three strong near-infrared bands due to spin-allowed transitions and for a number of weak sharp bands in the visible due to spin-forbidden
transitions. A quantitative assignment for the bands in the near-infrared and visible region of Fe(II)-bearing garnet has recently been achieved /6/ having considered the actual symmetry $D_2$ of the ions surrounding the Fe(II). The results show that the low symmetry contribution, which plays an important role in the complexity of the spectra, is large and should not be neglected. So, to predict the pressure shifts of the bands, we should consider the actual $D_2$ crystal field rather than the cubic field only. It should also be emphasized that predicting the pressure shifts requires exact assignment of the absorption bands and that, on the other hand, the theoretically predicted shifts would be expected as a useful method for identifying the specific transitions by comparison with the experimental findings.

The crystal field theory is commonly assumed to provide a reasonable description of metal ions in crystals which are ionic. Several results, however, have already shown that Fe(II) at garnet $D_2$ site is of highly ionic nature /7/ and that the predominantly contribution to the crystal field in this system appears to arise from ions in the first coordination sphere /8/. Therefore the superposition model and point-charge ionic bonding model are appropriate to calculate the energy levels of Fe(II) in garnet. Now according to the results of /6/, a purely theoretical approach to pressure shifts are performed.

Under the point-charge ionic bonding model, Fe(II), with $3d^6$ configuration, is subjected to the $D_2$ crystal field potential

$$ V = \sum_{i=1}^{6} V_i = \sum_{i=1}^{6} \sum_{k=1,2,3} \sum_{l=0}^{4} r_i^{\delta(l,\nu)} \phi_l(\theta_i, \varphi_i) $$

$$ = \frac{1}{\sqrt{3}} \beta \frac{1}{R_4} r_\theta Z_{20}(\theta_i, \varphi_i) + \frac{1}{\sqrt{15}} \epsilon \frac{1}{R_4} r_\theta Z_{12}(\theta_i, \varphi_i) + \frac{1}{\sqrt{2}} \beta \frac{1}{R_4} r_\theta Z_{20}(\theta_i, \varphi_i) $$

$$ + \frac{1}{\sqrt{15}} \epsilon \frac{1}{R_4} r_\theta Z_{12}(\theta_i, \varphi_i) + \frac{1}{\sqrt{35}} \epsilon \frac{1}{R_4} r_\theta Z_{44}(\theta_i, \varphi_i), $$

where $e$, $\nu$, $\delta$, $\epsilon$ can be calculated from the parameters of lattice; $Z_{2\ell}^{(b)}(\theta_i, \varphi_i)$ denotes real spherical harmonic functions; $r_i$, $\theta_i$, $\varphi_i$ are coordinates of d-electron on Fe(II); $e$ the proton charge; $q$ the equivalent charge of the ligand $O^2-$. Using the proper basis functions of $D_2$ symmetry, we obtain the Hamiltonian matrix elements of the triplet states $^3A_1$ (9 x 9 matrix), $^3B_2$, $^3B_3$ (12 x 12 matrices) and of the quintet states $^5A_1$ (2 x 2 matrices), $^5B_1$, $^5B_2$, $^5B_3$ (1 x 1 matrices). The matrix elements are expressions of the Racah parameters $B$, $C$, the Trees correction $\alpha'$, and the crystal field parameters which are the functions of expectation values $<r^2>$, $<r^4>$ and crystalline parameters. Because Zhao and Du's d-orbital for Fe(II) /1/ has been employed, the expectation values of $r^2$, $r^4$ and Racah parameters $B$, $C$ can be theoretically obtained: $<r^2> = 2.2949$ (a.u.), $<r^4> = 14$ (a.u.), $B = 947$ cm$^{-1}$, $C = 3375$ cm$^{-4}$. Thus the relation between d-d transitions of Fe(II) in garnet and its crystalline parameters can be established by solving several determinants.

As for the superposition model, the equation for the crystal field parameters at garnet $D_2$ site is of the form

$$ A_n^m < r^m > = \overline{A}_n^m (R) \left[ K_n^m (A) + \frac{R A}{R_B} t_2 K_n^m (B) \right], $$

where $K_n^m (A)$, $K_n^m (B)$ can be calculated from the angular coordinate; $\overline{A}_n^m (R)$ are intrinsic parameters which can be got by employing $d$-orbital for Fe(II) /1/; $t_2$ are power law exponents. With the power law exponents /6/ $t_2 = 3$, $t_4 = 7$, the geometric parameters $\alpha$, $\beta$, $\nu$, $\delta$ and $\epsilon$ are of the form

$$ \alpha = 8 \left[ K_4^O (A) + \frac{R A}{R_B} K_4^O (B) \right], \quad \beta = 2 \left[ K_2^O (A) + \frac{R A}{R_B} K_3^O (B) \right], $$

$$ \epsilon = \frac{1}{\sqrt{3}} R A \left[ K_3^O (A) + \frac{R A}{R_B} K_4^O (B) \right], $$

$$ \delta = \frac{1}{\sqrt{15}} R A \left[ K_3^O (A) + \frac{R A}{R_B} K_4^O (B) \right], $$

$$ \nu = \frac{1}{\sqrt{2}} R A \left[ K_3^O (A) + \frac{R A}{R_B} K_4^O (B) \right], $$

$$ \epsilon = \frac{1}{\sqrt{35}} R A \left[ K_3^O (A) + \frac{R A}{R_B} K_4^O (B) \right]. $$
Similarly, the energy levels of Fe(II) in garnet can be obtained as long as we know the crystalline parameters. Since Fe(II) in garnet is of highly ionic nature \cite{6,7}, it is expected that the change of the crystal structure plays an important role in the shifts of crystal bands. The unit-cell volume (Å³) and pressure (kbar) have the relation \cite{9}: 

\[ V_{\text{pyrope}} = 1503.5 - 1.13P + 0.004P^2 \].

Under the assumption that there are no internal distortion of the crystal structure apart from the uniform compression, we get, finally, the theoretically predicted pressure shifts without introducing any new parameters. The Fig. in next page shows the prediction in comparison with the experimental data \cite{10,11}.

II - DISCUSSION

The near-infrared bands of Fe(II) in crystals are strong spin-allowed transitions that arise from the same energy level $^3D$ and that, consequently, are independent of Racah parameters $B$, $C$. So the pressure shifts of ferrous bands in the near-infrared are a measure of crystal field. The predicted slope is close agreement with Balchan and Drickamer's \cite{11} and only a little greater than that reported in \cite{10}, as shown in Fig.(a). So it can be said that the relation we obtained between crystal field parameters for garnet $D_2$ symmetry and its crystalline parameters is a reasonable one which is fundamental to theoretical explanation of other bands in the visible.

The visible bands are spin-forbidden transitions that are the functions of crystal field parameters, Racah parameters and Trees correction. As shown in Fig.(b,c,d), the agreement of predicted shifts with experiments shows that the Racah parameters change very little with pressure, which is in accordance with the fact that Fe(II) in many silicate minerals is highly ionic \cite{6,12,13}. This implies that the ionic model for Fe(II)-O bond in garnet still holds at the pressure up to 50 kbar.

Generally, it is expected that the absorption bands would shift to higher energy with increasing crystal field parameters \cite{14}. But the predicted shifts of the band at 17600 cm$^{-1}$ is to lower energy, which is quantitatively agreement with the experiment, with increasing pressure, i.e., with increasing crystal field parameters. This indicates that the relation between the d-d transitions and the parameters of low symmetry crystal field is complicated rather than simple $Dq \propto R^2$.

As shown in Fig.(a,b,c,d), the blue-shift of the band 7800 cm$^{-1}$, the red-shift of the band 17600 cm$^{-1}$ and the nearly-zero-shifts of the bands 19100, 19800, 21600 cm$^{-1}$ have been well interpreted. This implies that:

1) the definite assignment in our earlier work of the spectrum of Fe(II) in garnet is reasonable,

2) the change of crystal structure plays the main role in the shifts of crystal bands and, especially, the main contribution to the shifts of spin-forbidden transitions is still the change of crystal structure rather than the decrease of Racah parameters which is generally regarded at present.

and 3) Fe(II) at dodechedral $D_2$ site is still of highly ionic nature at the pressure up to 50 kbar.
Fig. - Theoretical predicted shifts comparison with the experimental findings. The results obtained from two models are nearly the same. Line-1 corresponds to the theoretical predicted shifts, line-2 to the experimental findings from /lo/, line-3 to the results from /11/.

References
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