

## Superposition model analysis of the near infrared spectrum of Fe<sup>2+</sup> in pyrope-almadine garnets

DOUGLAS J. NEWMAN, DONALD C. PRICE AND W. ALAN RUNCIMAN

Department of Solid State Physics  
Research School of Physical Sciences  
Australian National University  
Canberra, A.C.T. 2600, Australia

### Abstract

The superposition model has been used to compare all possible assignments of group theoretical labels appropriate to the near infrared spectral bands of Fe<sup>2+</sup> in *D*<sub>2</sub> sites in pyrope garnet. A unique assignment is determined for the optical absorption bands at 7800, 6100 and 4500 cm<sup>-1</sup> to transitions from an *A* ground state to *B*<sub>2</sub>, *A*, and *B*<sub>3</sub> excited states respectively, contrary to the previous assignments of White and Moore (1972) and Runciman and Sengupta (1974).

### Introduction

The near infrared spectrum of Fe<sup>2+</sup> in silicate garnets consists of three strong bands. These bands exist with only slight change in position for the whole range of pyrope-almadine garnets (White and Moore, 1972, and earlier references in that paper). They are attributed to spin-allowed transitions between the <sup>5</sup>*D* levels of the 3*d*<sup>6</sup> configuration split in the crystal field of the slightly distorted cubal, or dodecahedral, site. White and Moore assigned these three bands, in order of decreasing energy, to transitions from the *A* ground state to the *B*<sub>2</sub>, *B*<sub>3</sub>, and *A* levels (using the group theoretical labels for *D*<sub>2</sub> symmetry). This will be termed the *B*<sub>2</sub>*B*<sub>3</sub>*A* assignment. Runciman and Sengupta (1974) proposed a *B*<sub>3</sub>*B*<sub>2</sub>*B*<sub>1</sub> assignment on the basis of group theoretical selection rules for the transition intensities. Huggins (1975) compared these assignments and rejected that of Runciman and Sengupta on the basis of Mössbauer data, which indicate that the two lowest states are separated by less than 2000 cm<sup>-1</sup>. This led him to favour the White and Moore assignment.

Huggins (1975) remarked that the dominant contributions to the crystal field in this system appear to arise from ions in the first coordination sphere. In this work we employ the superposition model, which puts this idea into quantitative terms, allows for covalency and overlap as well as electrostatic contributions, and produces parameters which can be related

to experimental results for other systems. We shall show that this approach to the problem is sufficient to select a unique state labelling out of the 24 possible assignments allowed if we accept the Mössbauer evidence for an *A* ground state (Prandl and Wagner, 1971; Dodokin *et al.*, 1972).

### Superposition model

The use of the superposition model to analyze the crystal field parameters of lanthanide ions in *D*<sub>2</sub> sites of various garnets has been described by Newman and Stedman (1969). In the present work we carry out a similar analysis for the Fe<sup>2+</sup> spectrum at *D*<sub>2</sub> sites in pyrope garnet, with the aim of providing a positive identification of the electronic transitions involved in generating the main features observed in the optical spectrum.

The main assumptions of the superposition model are

(i) Only the coordinated ions (or ligands) contribute significantly to the crystal field.

(ii) The contribution of each ligand is axially symmetric and depends only on its distance from the paramagnetic ion.

(iii) The total crystal field can be constructed simply by adding all the separate ligand contributions. This model is more restrictive than the electrostatic model in that it neglects contributions from all but the coordinated ions. At the same time the superposition model makes no assumptions about the

mechanism (or magnitude) of the ligand contributions.

In calculating the individual ligand contributions, angular factors are determined from the ionic positions given by X-ray data. The single ligand contributions are treated as undetermined functions (of the ligand distance  $R$ ) which must be fitted to the spectroscopic data. We shall assume, as is usual, that these functions  $A_n(R)$  take the form of an inverse power law ( $1/R^{t_n}$ ). This puts no restriction on the present calculation as only two ligand distances are involved.

The superposition model equation for the crystal field parameters at garnet  $D_2$  sites takes the simple form

$$A_n^m \langle r^n \rangle = \bar{A}_n \left\{ K_n^m(1) + \left( \frac{R_1}{R_2} \right)^{t_n} K_n^m(2) \right\}$$

where  $R_1$  is the nearest-neighbour distance,  $R_2$  is the next-nearest-neighbour distance and  $K_n^m(1)$ ,  $K_n^m(2)$  can be calculated from the angular coordination (Newman and Urban, 1975, p. 816). Stevens' normalization of the crystal-field parameters is employed (Stevens, 1952; Elliott and Stevens, 1952). They are related to the  $B_n^m$  parameters of Runciman and Sengupta (1974) by

$$B_2^0 = 2A_2^0 \langle r^2 \rangle, B_2^2 = \sqrt{\frac{2}{3}} A_2^2 \langle r^2 \rangle, B_4^0 = 8A_4^0 \langle r^4 \rangle$$

$$B_4^2 = 2\sqrt{\frac{2}{5}} A_4^2 \langle r^4 \rangle, B_4^4 = 4\sqrt{\frac{2}{35}} A_4^4 \langle r^4 \rangle$$

Table 1 gives the ionic positions used by Runciman and Sengupta (1974) and the derived coordination factors for pyrope garnet. Values for YAG are also given (Newman and Stedman, 1969; Newman and Edgar, 1976), to emphasize the close similarity between the sites in these two systems. The absorption spectrum shows three distinct transitions, at 7800  $\text{cm}^{-1}$ , 6100  $\text{cm}^{-1}$ , and 4500  $\text{cm}^{-1}$  (e.g. Runciman and Sengupta, 1974). Since all the observed transitions are vibronic, these numbers only give an approximate measure of the electronic energy levels. Five phenomenological crystal-field parameters are required to specify the electronic states, so that a model of the crystal field is required to reduce the number of parameters to three. In the superposition model four parameters are required to specify the crystal field acting upon  $3d^N$  states, the intrinsic parameters  $\bar{A}_2$ ,  $\bar{A}_4$ , and the power law exponents  $t_2$  and  $t_4$ . In order to reduce this number to three we shall assume that  $t_4 = 5$ , for which there is some experimental and theoreti-

Table 1. Ionic positions and coordination factors for the  $D_2$  sites in pyrope garnet and yttrium aluminium garnet (YAG) compared with the corresponding contributions in cubic symmetry

	R (Å)	$\theta^\circ$	$\phi^\circ$	$K_2^0$	$K_2^2$	$K_4^0$	$K_4^2$	$K_4^4$
Pyrope garnet	2.20	57	12	-0.22	3.86	-1.41	6.92	5.79
	2.34	55	80	-0.03	-3.78	-1.54	-8.22	6.04
YAG	2.30	56.1	12.5	-0.14	3.75	-1.47	7.32	5.34
	2.43	54.1	80.9	0.37	-3.75	-1.59	-8.82	6.16
Cubic		54.74	0.0	0	4.00	-1.56	8.89	7.77
		54.74	90.0	0	-4.00	-1.56	-8.89	7.77

cal evidence (e.g., see Stedman, 1969). It is convenient to use  $A_2^0 \langle r^2 \rangle$  and  $A_2^2 \langle r^2 \rangle$  as fitting parameters, avoiding the use of the superposition model for  $n = 2$ , which is expected to be relatively inaccurate in this case because of a larger electrostatic contribution. Although this model makes it possible in principle to obtain the crystal field parameters from the spectrum, in fact sixty distinct sets of parameters can be obtained unless the group theoretical state labels are known.

Mössbauer measurements on magnetically-ordered almandine garnets (e.g. Prandl and Wagner, 1971; Dodokin *et al.*, 1972; Routcliffe, 1976) give both the sign and magnitude of the principal components of the electric field gradient at the nucleus of an  $\text{Fe}^{2+}$  ion in a dodecahedral site. These values indicate unequiv-

Table 2. Parameters obtained for the 24 alternative superposition model fits to experimental data based on the assumption of an  $A$  ground state. All quantities are given in  $\text{cm}^{-1}$

Identification*	Level not observed	$\bar{A}_4$	$A_2^0 \langle r^2 \rangle$	$A_2^2 \langle r^2 \rangle$
$B^2AB^3$	$E(B^1) = 1100$	596	-175	5075
$B_2B_3A$	< 0			
$B_3B_2A$	< 0			
$AB_2B_3$	= 600	-70	6197	2882
$B_3AB_2$	= 800	554	603	-6426
$AB_3B_2$	= 600	-70	6197	-2718
$B_1B_2B_3$	$E(A) = 10600$	351	-6485	2388
$B_1B_3B_2$	= 10600	351	-6485	-3212
$B_2B_1B_3$	= 10000	477	-4795	5215
$B_3B_1B_2$	= 10100	456	-4581	-6310
$B_2B_3B_1$	= 9300	625	-3494	2242
$B_3B_2B_1$	= 9400	604	-3280	-3683
$B_1B_3A$	$E(B_2) < 0$			
$B_1AB_3$	< 0			
$B_3B_1A$	< 0			
$AB_1B_3$	= 2400	183	-4947	-3889
$B_3AB_1$	< 0			
$AB_3B_1$	= 3800	379	-3329	-4470
$B_1B_2A$	$E(B_3) < 0$			
$B_1AB_2$	< 0			
$B_2B_1A$	< 0			
$AB_1B_2$	= 2500	197	-5032	3269
$B_2AB_1$	< 0			
$AB_2B_1$	= 4000	407	-3498	3197

\*These give the observed spectral lines in order of decreasing energy, so that  $B_1B_2B_3$  signifies  $E(B_1) = 7800 \text{ cm}^{-1}$ ,  $E(B_2) = 6100 \text{ cm}^{-1}$ ,  $E(B_3) = 4500 \text{ cm}^{-1}$ , relative to the ground level  $E(A) = 0$ .

ocally that the ionic ground state is derived predominantly from the  $3z^2-r^2$  orbital and transforms as  $A$ . This is consistent with the fact that the garnet  $D_2$  sites are only slightly distorted from cubic symmetry, so that the ground state must be either  $A$  or  $B_1$  (as the cubic ground state  $E \rightarrow A + B_1$ ). This constraint allows twenty-four different identifications of the remaining levels. The results of fitting the parameters for all these cases are shown in Table 2.

It will be seen from Table 2 that 10 of the 24 cases considered do not provide a consistent fit to the data. We shall seek to discriminate between the remaining fits by means of the following criteria:

(i)  $\bar{A}_4 > 0$ , and should take a value similar to that for  $3d^N$  ions at cubic sites with oxygen ligands. The work of Manson *et al.* (1976) on  $\text{Fe}^{2+}:\text{MgO}$  provides a value of  $\bar{A}_4 = 701 \text{ cm}^{-1}$ , which scales to  $\bar{A}_4 = 564 \text{ cm}^{-1}$  in the garnet with  $t_4 = 5$ . This prediction should be accurate to within 10 percent.

(ii) The temperature-dependence of the  $^{57}\text{Fe}$  nuclear quadrupole splitting in  $\text{Fe}^{2+}$  ions in dodecahedral sites in almandine and pyrope garnets was measured by Lyubutin and Dodokin (1970) and Amthauer *et al.* (1976) respectively. In both cases the decrease in the magnitude of the splitting with increasing temperature was interpreted on the assumption that the lowest excited orbital state was  $B_1$ , as would be expected for a small distortion from cubic symmetry, and the excitation energy of this state was deduced to be  $1070 \text{ cm}^{-1}$  and  $1150\text{--}1200 \text{ cm}^{-1}$  respectively. These estimates would remain unchanged if the excited state was the other  $A$  level ( $x^2-y^2$ ), but if either  $B_2$  or  $B_3$  were the lowest excited state then the experimental data show the energy to be considerably less than  $1000 \text{ cm}^{-1}$ . Other factors such as the temperature-dependence of the crystal field and possible effects of vibronic coupling (Price, in preparation) make estimation of the excitation energy of the first excited state to better than about 50 percent difficult. We therefore estimate the energy of the lowest lying level to be  $1100 \text{ cm}^{-1} \pm 50$  percent.

(iii) The coordination factors in Table 1 suggest that  $A_2^0 \langle r^2 \rangle$  is positive, which is certainly true in other garnet systems (*e.g.*, see Newman and Edgar, 1976). Similar evidence indicates that  $A_2^0 \langle r^2 \rangle$  is negative and smaller in magnitude than  $A_2^0 \langle r^2 \rangle$ .

Using each of the criteria in turn, we list the acceptable fits as follows:

- (i)  $B_2AB_3, B_3AB_2, B_2B_3B_1, B_3B_2B_1$
- (ii)  $B_2AB_3, AB_2B_3, B_3AB_2, AB_2B_2$
- (iii)  $B_2AB_3, B_2B_1B_3.$

The only fit which satisfies all three criteria is seen to be  $B_2AB_3$ , which is the first listed in Table 2. It should be noted, however, that  $B_3AB_2$  satisfies two of the criteria and should therefore not be rejected without further consideration. In this regard it must be emphasised that criterion (iii) is very far from being satisfied by  $B_3AB_2$ , as the signs of both  $A_2^0 \langle r^2 \rangle$  and  $A_2^0 \langle r^2 \rangle$  are incorrect. Also  $E(B_1)$  lies near the lowest acceptable value on criterion (ii). These extra factors confirm our rejection of this fit.

To provide an additional check on  $B_2AB_3$  as the only possible identification of the observed excited-state energy levels, we now estimate the superposition model parameters  $\bar{A}_2, t_2$  in this case. Newman and Edgar (1976) have shown that  $K_2^0$  is very sensitive to local distortion effects, so we shall ignore the parameter in  $A_2^0 \langle r^2 \rangle$  in this analysis. If we assume  $t_2 = 3$ , the value of  $A_2^0 \langle r^2 \rangle$  gives  $\bar{A}_2 = 7060 \text{ cm}^{-1}$ , while for  $t_2 = 4$ ,  $\bar{A}_2 = 5590 \text{ cm}^{-1}$ . These may be compared with the value of  $\bar{A}_2 = 5507 \text{ cm}^{-1}$  for  $\text{Co}^{2+}$  in  $\text{CdCl}_3$  obtained by Edgar (1976).

### Conclusion

Use of the superposition model in conjunction with Mössbauer data has allowed us to give a definite assignment of the optical transitions of  $\text{Fe}^{2+}$  at  $D_2$  sites in pyrope garnet. This identification ( $B_2AB_3$ ) does not accord with the identification  $B_2B_3A$  previously proposed by White and Moore (1972), nor with the identification  $B_3B_2B_1$  proposed by Runciman and Sengupta (1974). It is, however, in agreement with the identification proposed, but not substantiated in detail, by Routcliffe (1976).

The superposition model parameter  $t_4$  has been assumed to take the value  $t_4 = 5$ , allowing us to derive a value  $\bar{A}_4 = 596 \text{ cm}^{-1}$  in good accord with the value extrapolated from the MgO data of Manson *et al.* (1976),  $\bar{A}_4 = 564 \text{ cm}^{-1}$ . The derived value of  $\bar{A}_2$  is much less certain, but of interest in view of the very few determinations of this quantity that have been made for  $3d^N$  systems. Taking the most likely range of  $t_2$  to be  $t_2 = 3.5 \pm 0.5$ , we obtain  $\bar{A}_2 = 6300 \pm 800 \text{ cm}^{-1}$ . The ratio  $\bar{A}_2/\bar{A}_4$  is greater than that found for lanthanide ions, presumably due to the relatively small effect of electrostatic screening in  $\text{Fe}^{2+}$ .

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