Theoretical calculations of the spin-lattice coupling coefficients G_{11} and G_{44} for MgO:Ni^{2+} crystals

Zheng Wen-Chen
*China Center of Advanced Science and Technology (World Laboratory), P.O. Box 8730, Beijing, China and Department of Material Science, Sichuan University, Chengdu 610064, People's Republic of China**
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The analytic expressions of spin-lattice coupling coefficients G_{11} and G_{44} in cubic symmetry for d^8 ions are put forward from a unified method suitable to all d^n ions and the high-order perturbation formulas of zero-field splittings for d^8 ions in tetragonal and trigonal symmetries. According to the expressions, the coefficients G_{11} and G_{44} for MgO:Ni^{2+} crystals have been calculated from the point-charge model by using only one adjustable parameter N (average covalency reduction factor) obtained from the optical absorption spectra. The results are in good agreement with the experimental findings.

INTRODUCTION

The spin-lattice coupling coefficients or magnetoelastic coupling coefficients G_{11} and G_{44} for MgO:Ni^{2+} crystals were measured from the uniaxial stress experiments of EPR spectra several decades ago,[1] but the theoretical explanation of them is still in a state of confusion. In particular, all the theoretical results given by the previous authors[2-5] are that $G_{11} < G_{44}$ whereas the experimental values are that $G_{11} > G_{44}$ (see Table I). This shows that these theoretical treatments are not successful and so the problem needs further studies. In this paper, we will deal with this problem by using the unified method of obtaining the expressions of the coefficients G_{11} and G_{44} for d^n ions from the formulas of zero-field splittings in tetragonal and trigonal symmetries, respectively,[6] and use them for d^8 ions to calculate the coefficients G_{11} and G_{44} for MgO:Ni^{2+} crystals. The results are consistent with the experimental values.

CALCULATION

When a d^n ion is placed in a strain field (e_{kl}), a zero-field splitting $\bar{\mathbf{S}}\cdot\vec{D}\cdot\bar{\mathbf{S}}$ arises with

$$D_{ij} = \sum_{k,l} G_{ijkl} e_{kl} , \tag{1}$$

as a consequence of the reduction of local symmetry. Obviously, there are only two dependent coupling coefficients G_{11} and G_{44} in a cubic lattice. When stress P ($P > 0$) is along the [001] axis of cubic crystals, the zero-field splitting due to induced tetragonal distortion is[3,7]

$$dD/dP = -\tfrac{3}{2} G_{11}(s_{11} - s_{12}) , \tag{2}$$

where s_{ij} is the element of the compliance tensor.

If $R_\parallel$ and $R_\perp$ stand for the bonding lengths parallel to and perpendicular to the axis of fourfold rotation, respectively, the tetragonal distortion can be represented by the angle α which is defined as

$$\tan\alpha = R_\perp/R_\parallel = \frac{R_0(1 - s_{12}P)}{R_0(1 - s_{11}P)} . \tag{3}$$

For cubic symmetry, $\alpha = \alpha_0 = 45°$. Obviously,

$$d\alpha/dP = \tfrac{1}{2}(s_{11} - s_{12}) . \tag{4}$$

Considering that

$$dD/dP = (\partial D/\partial\alpha)_0(\partial\alpha/\partial P) , \tag{5}$$

from (2)-(5), we have

$$G_{11} = -\tfrac{1}{3}(\partial D/\partial\alpha)_0 , \tag{6}$$

where the zero subscript denotes that the differentiation is done for the case of cubic symmetry.

Similarly, when stress P is along the [111] axis, the trigonal distortion arises, then[3,7]

$$dD/dP = -G_{44}s_{44} . \tag{7}$$

For the trigonal distortion β (where β denotes the angle between the direction of metal-ligand pair and the C_3 axis, in the cubic crystal, $\beta = \beta_0 = 54.74°$), we have

$$d\beta/dP = \frac{\sqrt{2}}{6} s_{44} , \tag{8}$$

so,

$$G_{44} = -\sqrt{2}/6(\partial D/\partial\beta)_0 . \tag{9}$$

Obviously, the coefficients G_{11} and G_{44} can be calculated very easily from the derivatives of zero-field splitting in tetragonal and trigonal fields with respect to the distinctive distortion angles. The unified method is applicable to all d^n ions[6] and simpler than the usual one of calculating directly from the strain tensor elements.

TABLE I. Spin-lattice coupling coefficients G_{11} and G_{44} for MgO:Ni^{2+} (in units of cm^{-1} per unit strain).

	G_{11}	G_{44}
Brog and Ray (Ref. 2)	46.4	88.5
Zdansky (Ref. 3)	43	58
Tucker (Ref. 4)	46.6	90.7
Tucker (Ref. 5)	36.9	46.5
This work	53	41
Experiment (Ref. 1)	57 ± 8	36 ± 5

Let us use the method for d^8 ions. The high-order perturbation formula of zero-field splitting D for d^8 ions in tetragonal symmetry from the strong-field coupling scheme can be obtained from that in rhombic field[8] (i.e., let angle $\phi=90°$):

$$D=\tfrac{35}{4}\xi_d^2 D_t\left(\frac{1}{W_2^2}-\frac{1}{W_1^2}\right)+\tfrac{9}{2}\xi_d^3(D_s+\tfrac{4}{5}D_t)\left(\frac{1}{W_1W_2W_3}-\frac{1}{W_1^2W_3}\right)+\tfrac{35}{8}\xi_d^3 D_t\frac{1}{W_1^3}+\tfrac{2695}{16}\xi_d^2 D_t^2\left(\frac{1}{W_2^3}-\frac{1}{W_1^3}\right)$$
$$+3\xi_d^2(D_s+\tfrac{5}{4}D_t)^2\left(\frac{1}{W_1^2W_3}-\frac{1}{W_2^2W_6}\right)+\tfrac{35}{8}\xi_d^3 D_t\left(\frac{2}{W_1W_2^2}-\frac{1}{W_1^2W_2}\right), \tag{10}$$

where ξ_d, D_s, and D_t are defined in Ref. 8 and the zero-order energy separations are

$$W_1=\Delta,\quad W_2=\Delta+8B+2C,\quad W_3=\Delta+12B,$$
$$W_4=2\Delta+3B,\quad W_5=2\Delta+9B+2C,\quad W_6=\Delta+12B+2C. \tag{11}$$

So, the analytic expression of G_{11} is

$$G_{11}=-\tfrac{1}{3}(\partial D/\partial\alpha)_0=\tfrac{35}{12}\xi_d^2\left(\frac{1}{W_1^2}-\frac{1}{W_2^2}\right)(\partial D_t/\partial\alpha)_0+\tfrac{3}{2}\xi_d^3\left(\frac{1}{W_1^2W_3}-\frac{1}{W_1W_2W_3}\right)[(\partial D_s/\partial\alpha)_0+\tfrac{4}{5}(\partial D_t/\partial\alpha)_0]$$
$$+\tfrac{35}{24}\xi_d^3\left(\frac{1}{W_1^2W_2}-\frac{2}{W_1W_2^2}-\frac{1}{W_1^3}\right)(\partial D_t/\partial\alpha)_0, \tag{12}$$

with

$$(\partial D_t/\partial\alpha)_0=\tfrac{40}{7}Dq,\quad (\partial D_s/\partial\alpha)_0=-\tfrac{12}{7}eq\langle r^2\rangle/R_0^3, \tag{13}$$

from the definitions of parameters D_t and D_s (Ref. 8) and the point-charge model. q is the charge of ligands.

For the trigonal field, the high-order perturbation formula of the splitting D from strong-field coupling scheme is[9]

$$D=\frac{\xi_d^2 v}{2}\left(\frac{1}{W_1^2}-\frac{1}{W_2^2}\right)+\frac{3\sqrt{2}}{2}\xi_d^2 v'\left(\frac{1}{W_2W_3}-\frac{1}{W_1W_3}\right)$$
$$+6\sqrt{2}B\xi_d^2 v'\left(\frac{1}{W_2W_3W_5}+\frac{1}{W_2^2W_5}-\frac{3}{W_1W_3W_4}-\frac{3}{W_2W_3W_4}\right), \tag{14}$$

then

$$G_{44}=-\frac{\sqrt{2}}{6}(\partial D/\partial\beta)_0=\frac{\sqrt{2}}{12}\xi_d^2\left(\frac{1}{W_2^2}-\frac{1}{W_1^2}\right)(\partial v/\partial\beta)_0+\frac{\xi_d^2}{2}\left(\frac{1}{W_1W_3}-\frac{1}{W_2W_3}\right)(\partial v'/\partial\beta)_0$$
$$-2B\xi_d^2\left(\frac{1}{W_2W_3W_5}+\frac{1}{W_2^2W_5}-\frac{3}{W_1W_3W_4}-\frac{3}{W_2W_3W_4}\right)(\partial v'/\partial\beta)_0. \tag{15}$$

From the expressions of the trigonal-field parameters v and v' (Ref. 10) and the point-charge model, we have

$$(\partial v/\partial\beta)_0=\frac{18\sqrt{2}}{7}eq\langle r^2\rangle/R_0^3+\frac{60\sqrt{2}}{7}Dq,$$
$$(\partial v'/\partial\beta)_0=-\frac{12}{7}eq\langle r^2\rangle/R_0^2+\frac{30}{7}Dq. \tag{16}$$

So, from the above formulas the coefficients G_{11} and G_{44} of d^8 ions can be calculated easily.

Now we focus attention on the Ni^{2+} ion in the MgO crystal. Utilizing the empirical d orbital of the Ni^{2+} ion obtained from a great many optical spectra for the crystals containing Ni^{2+} ions, we have[11]

$$R_d(r)=0.73948[O(5.511)]+0.50000[O(1.5746)], \tag{17}$$

where O denotes a Slater orbital. So,

$$B_0=1208\ \text{cm}^{-1},\quad C_0=4459\ \text{cm}^{-1},\quad \xi_{d0}=636\ \text{cm}^{-1},$$
$$\langle r^2\rangle_0=1.8904\ \text{a.u.},\quad \langle r^4\rangle_0=13.4043\ \text{a.u.} \tag{18}$$

Introducing a parameter N to denote the average covalency reduction, we get

$$B=N^4B_0,\quad C=N^4C_0,\quad \xi_d=N^2\xi_{d0},\quad \langle r^k\rangle=N^2\langle r^k\rangle_0. \tag{19}$$

From the optical spectra of MgO:Ni^{2+} crystals,[12,13] one can obtain $N=0.943$. The comparison of spectra between theory and experiments is given in Table II. Substituting the parameter N and the structural datum $R_0=2.1$ Å of the MgO crystal into the above formulas, we obtain

$$G_{11}=53,\quad G_{44}=41 \tag{20}$$

TABLE II. *d-d* transition in $MgO:Ni^{2+}$ crystal.

Transition	Theoretical frequency (cm^{-1})	Experimental frequency[a] (cm^{-1})
$^3A_2(F) \rightarrow {}^3T_2(F)$	8845	8600, 8845
$\rightarrow {}^1E(D)$	14108	13700
$\rightarrow {}^3T_1(F)$	14700	14700
$\rightarrow {}^1T_2(D)$	22510	21550, 21715
$\rightarrow {}^3T_1(P)$	26147	24500
$\rightarrow {}^1A_1(G)$	24008	25900
$\rightarrow {}^1T_1(G)$	27337	28300
$\rightarrow {}^1E(G)$	33888	
$\rightarrow {}^1T_2(G)$	34330	34500
$\rightarrow {}^1A_1(S)$	57816	

[a]References 12 and 13.

in units of cm^{-1}/unit strain. Obviously, our results show good agreement with the experimental findings (see Table I).

CONCLUSION

In conclusion, our method can remove the theoretical difficulty about the spin-lattice coupling coefficients in the $MgO:Ni^{2+}$ crystal, and explain the optical spectra as well in a unified way by using only one parameter N. The method should also be effective for other similar cases.

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*Mailing address.

[1]G. D. Watkins and E. R. Feher, Bull. Am. Phys. Soc. **7**, 29 (1962).
[2]M. Borg and D. K. Ray, Phys. Rev. B **1**, 4144 (1970).
[3]K. Zdansky, Phys. Rev. **159**, 201 (1967).
[4]E. B. Tucker, Phys. Rev. **143**, 264 (1966).
[5]E. B. Tucker, Proc. IEEE **53**, 1547 (1965).
[6]W. C. Zheng, Phys. Lett. A **137**, 309 (1989).
[7]E. R. Feher, Phys. Rev. **136**, A145 (1964).
[8]J. J. Chen and M. G. Zhao, Phys. Status Solidi (b) **143**, 647 (1987).
[9]A. K. Petrosyan and A. A. Mirzakhanyan, Phys. Status Solidi (b) **133**, 315 (1986).
[10]W. C. Zheng, Phys. Rev. B **36**, 8774 (1987).
[11]Q. Xiong, G. R. Bai, and M. G. Zhao, J. Appl. Phys. **57**, 3739 (1985).
[12]W. Low, Phys. Rev. **109**, 247 (1958).
[13]S. Minomura and H. G. Drickhamer, J. Chem. Phys. **35**, 903 (1961).