Studies of Zero-field Splitting and its Pressure and Stress Dependence for Ni^{2+} in $La_2Mg_3(NO_3)_{12} \cdot 24\ H_2O$ Crystal

Wen-Chen Zheng[a,b,c], Shao-Yi Wu[a,b,c], and Hui-Ning Dong[a]

[a] Department of Material Science, Sichuan University, Chengdu 610064, P. R. China
[b] International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, P. R. China
[c] Key Laboratory for Radiation Physics and Technology of the Ministry of Education, P. R. China (in Sichuan University)

Reprint requests to W.-C. Z; E-mail: zhengwenchen@netease.com

Z. Naturforsch. **56 a**, 855–858 (2001); received September 5, 2001

By using the high-order perturbation formulas, the g factors $g_{\|}$ and $g_{\perp}$, the zero-field splittings D and the pressure and uniaxial stress dependences of zero-field splitting are studied for Ni^{2+} ions in both Mg^{2+} sites of $La_2Mg_3(NO_3)_{12} \cdot 24\ H_2O$ crystal. It is found that the local trigonal distortion angles β_i of the two Ni^{2+} centers are only slightly different from the corresponding host ones, but the local angular compressibilities under pressure and stress for both Ni^{2+} centers are quite different not only from the corresponding host ones, but also from each other.

Key words: $La_2Mg_3(NO_3)_{12} \cdot 24\ H_2O$; Ni^{2+}; EPR; Local Distortion; Local Compressibility; Crystal Field Theory.

1. Introduction

$La_2Mg_3(NO_3)_{12} \cdot 24\ H_2O$ (LMN) belongs to a series of double nitrates having the generic formula 3 $[D(H_2O)_6]$ 2 $[T(NO_3)_6] \cdot 6\ H_2O$, where D is a divalent and T a trivalent cation. There are two different Mg^{2+} sites denoted by I (or X) and II (or Y) in LMN. Each Mg^{2+} is surrounded by a trigonally distorted octahedron of six water molecules. The local symmetry for the X site is D_{3d} and that for the Y site is C_{3v} [1]. The EPR parameters (g factors and zero-field splitting D) and the pressure and uniaxial stress (i. e., stress $U \parallel C_3$ axis) dependences of splitting D for Ni^{2+} in both Mg^{2+} sites of LMN were reported [2, 3], however, no satisfactory theoretical explanations have been made for them. In this paper, we study these EPR parameters and the pressure and stress dependences of zero-field splitting for both Ni^{2+} centers in LMN by high-order perturbation formulas. Based on the studies, the local trigonal distortion angles and the local angular compressibilities under pressure and stress are obtained. The results are discussed.

2. Calculations

For the Ni^{2+} (d^8) ion on a trigonal octahedral crystal site the fourth-order perturbation formulas of the EPR parameters $g_{\|}$, $g_{\perp}$ and D derived by the "quasi-intermediate-field" method are as follows [4]:

$$\begin{aligned} D &= \zeta^2(1/E_1^2 - 1/E_2^2)V/2 + (3/\sqrt{2})V' \\ &\quad \cdot \{\zeta^2[1/(E_2E_3) - 1/(E_1E_3)] + 4B\zeta^2[1/(E_2E_3E_5) \\ &\quad + 1/(E_2^2E_5) - 3/(E_1E_3E_4) - 3/(E_2E_3E_4)]\}, \\ g_{\|} &= g_s + 4k\zeta/E_1 - (g_s + k/2)\zeta^2/E_1^2 - (g_s - k/2) \\ &\quad \cdot \zeta^2/E_2^2 - k\zeta^2/(E_1E_2) - 6Bk\zeta^2[2/(E_1E_2E_5) \\ &\quad + 1/(E_2^2E_5)] - 4k\zeta V/(3E_1^2) \\ &\quad + 4\sqrt{2}\zeta V'k[1/(E_1E_3) + 12B/(E_1E_3E_4)], \\ g_{\|} &= g_{\perp} + 2k\zeta V/E_1^2 - 6\sqrt{2} \\ &\quad + \zeta V'k[1/(E_1E_3) + 12B/(E_1E_3E_4)] \end{aligned} \tag{1}$$

with

$$\begin{aligned} &E_1 = 10D_q,\ E_2 = 10D_q + 2C + 8B, \\ &E_3 = 10D_q + 12B,\ E_4 = 20D_q + 3B, \\ &E_5 = 20D_q + 2C + 9B, \end{aligned} \tag{2}$$

0932–0784 / 01 / 1200–0855 $ 06.00

where $g_s = 2.0023$. ζ is the spin-orbit coupling coefficient, k the orbital reduction factor, and D_q the cubic-field parameter. B and C are the Racah parameters, and V and V' the trigonal field parameters. From the superposition model [5] we have

$$V = \sum_{i=1}^{2}[(9/7)\overline{A}_2(R_0)(R_0/R_i)^{t_2}(3\cos^2\theta_i - 1)$$

$$+ (20/21)\overline{A}_4(R_0)(R_0/R_i)^{t_4}(35\cos^4\theta_i - 30\cos^2\theta_i + 3)$$

$$+ (20\sqrt{2}/3)\overline{A}_4(R_0)(R_0/R_i)^{t_4}\sin^3\theta_i\cos\theta_i],$$

$$V' = \sum_{i=1}^{2}[(-3\sqrt{2}/7)\overline{A}_2(R_0)(R_0/R_i)^{t_2}(3\cos^2\theta_i - 1)$$

$$+ (5\sqrt{2}/21)\overline{A}_4(R_0)(R_0/R_i)^{t_4}$$

$$\cdot (35\cos^4\theta_i - 30\cos^2\theta_i + 3)$$

$$+ (10/3)\overline{A}_4(R_0)(R_0/R_i)^{t_4}\sin^3\theta_i\cos\theta_i], \quad (3)$$

where R_i ($i = 1, 2$) and β_i are, respectively, the metal-ligand distance and the angle between the direction of R_i and the C_3 axis. t_2 and t_4 are the power-law exponents. We take $t_2 \approx 3$ and $t_4 \approx 5$ because of the ionic nature of bonds [5 - 7]. $\overline{A}_2(R_0)$ and $\overline{A}_4(R_0)$ are the intrinsic parameters with the reference distance $R_0 \approx (R_1 + R_2)/2$. For $3d^n$ ions in octahedra, $\overline{A}_4(R_0) \approx (3/4)D_q$ [6, 7], and $\overline{A}_2(R_0)/\overline{A}_4(R_0) \approx 9 \sim 12$ for $3d^n$ ions in many crystals [6 - 9]. We take $\overline{A}_2(R_0)/\overline{A}_4(R_0) \approx 12$ here.

Since the Ni^{2+} ions in $NiSiF_6 \cdot 6\ H_2O$ and LMN have the same $[Ni(H_2O)_6]^{2+}$ groups and similar metal-ligand distances R (note: for $NiSiF_6 \cdot 6\ H_2O$, $R \approx 2.048$ Å [10], for LMN:Ni^{2+}, $R \approx 2.058$ Å for the X site and $\overline{R} \approx 2.056$ Å for the Y site [1]), we can reasonably estimate the parameters D_q, B and C of LMN:Ni^{2+} from the optical spectra of $NiSiF_6 \cdot 6\ H_2O$ [11]. Thus, we have

$$D_q \approx 920\ cm^{-1}, B \approx 900\ cm^{-1}, C \approx 4020\ cm^{-1}. \quad (4)$$

Because of the covalency reduction effect, the parameters ζ and k in crystals can be estimated by the correlations [12]: $\zeta \approx N^2\zeta_0$, $k \approx N^2\ N^2 \approx [(B/B_0 + C/C_0)/2]^{1/2}$, where ζ_0, B_0, and C_0 are the corresponding parameters of the free $3d^n$ ion. For a free Ni^{2+} ion [13], $\zeta_0 \approx 649\ cm^{-1}$, $B_0 \approx 1084\ cm^{-1}$, and $C_0 \approx 4831\ cm^{-1}$. The structural data of the host LMN crystal for the X site are $R_1 = R_2 \approx 2.056$ Å, $\beta_1 = \beta_2 \approx 54.39°$, and for the Y site they are $R_1 \approx 2.048$ Å, $R_2 \approx 2.063$ Å, $\beta_1 \approx 54.43°$ and $\beta_2 \approx 56.04°$ [1]. Substituting these parameters into the above formulas, we calculate the EPR parameters $g_{\|}$, $g_{\perp}$ and D for Ni^{2+} in X and Y sites of an LMN crystal. The calculated values of D for both Ni^{2+} centers are in poor agreement with the observed values (see Table 1). Since the zero-field splitting D is sensitive to the trigonal distortion angles β_i, the above calculated results suggest that the local angles β_i in the two Ni^{2+} centers may be different from the host ones. Assuming that the local angle $\beta_i^l \approx \beta_i(1 + K_j)$ and fitting the calculated value of the zero-field splitting to the observed value, we obtain for the X center, $K_X \approx 0.005$, $\beta_1^l = \beta_2^l \approx 54.66°$, and for the Y center, $K_Y \approx 0.0061$, $\beta_1^l \approx 54.74°$, $\beta_2^l \approx 56.38°$. A comparison between the calculated and observed EPR parameters for both Ni^{2+} centers is shown in Table 1.

Table 1. EPR parameters and pressure and stress dependences of zero-field splitting for Ni^{2+} in both Mg^{2+} sites of $La_2Mg_3(NO_3)_{12} \cdot 24\ H_2O$.

	X site			X site		
	Cal.[a]	Cal.[b]	Expt.	Cal.[a]	Cal.[b]	Expt.
$g_{\|}$	2.25	2.25	2.24(1) [c]	2.24	2.24	2.25(1) [c]
$g_{\perp}$	2.26	2.25	2.24(1) [c]	2.23	2.22	2.25(1) [c]
D (cm^{-1})	0.94	0.2	0.200(5) [c]	−1.30	−2.22	−2.22(1) [c]
dD/dP ($10^{-3}cm^{-1}$/kBar)	84	433	432 [c,d]	117	188	188 [c,d]
dD/dU ($10^{-3}cm^{-1}$/kBar)	−368	−209	−210 [c,d]	−348	−103	−103 [c,d]

[a] Calculated by using the host structural data for the EPR parameters or by using the host compressibilities for dD/dP and dD/dU, [b] calculated by using the local structural data for EPR parameters or by using the local compressibilities for dD/dP and dD/dU, [c] [2], [d] [3].

Under the pressure P and uniaxial stress U ($U \| C_3$ axis) we have

$$R(P) \approx R[1 + (d\ln R/dP)P],$$

$$\beta(P) \approx \beta[1 + (d\ln\beta/dP)P],$$

$$R(U) \approx R[1 + (d\ln R/dU)U],$$

$$\beta(U) \approx \beta[1 + (d\ln\beta/dU)U], \quad (5)$$

where $d\ln R/dP$, $d\ln\beta/dP$, $d\ln R/dU$ and $d\ln\beta/dU$ are the bond and angular compressibilities under pressure and stress, respectively. Since the angles β_i in both centers are close to the angle β_0 ($\approx 54.74°$, the angle in a cubic octahedron), the compressibilities of the host crystal can be approximately calculated from

the elastic constants s_{ij} of the studied LMN crystal as follows [3, 14]:

$$\begin{aligned} d\ln R/dP &\approx -(2s_{11} + 2s_{12} + 4s_{13} + s_{33})/3 \\ &\approx -1.5 \times 10^{-3}\,(\text{kbar})^{-1}, \\ d\ln\beta/dP &\approx \sqrt{2}(s_{13} + s_{33} - s_{11} - s_{12})/3 \\ &\approx -0.58 \times 10^{-3}\,(\text{kbar})^{-1}, \\ d\ln R/dU &\approx -(2s_{13} + s_{33})/3 \\ &\approx -0.24 \times 10^{-3}\,(\text{kbar})^{-1}, \\ d\ln\beta/dU &\approx \sqrt{2}(s_{33} - s_{13})/3 \\ &\approx 2.50 \times 10^{-3}\,(\text{kbar})^{-1}. \end{aligned} \tag{6}$$

Applying these host compressibilities to the above formulas, we calculate the pressure and stress dependences of zero-field splitting for both Ni^{2+} centers in the LMN crystal. The results also disagree with the observed values (see Table 1), suggesting that the local compressibilities in the vicinity of the Ni^{2+} ion are different from those in the bulk crystal. In the calculations we find that the zero-field splitting D is sensitive to the angle β_i but insensitive to the distances R_i. For simplicity we assume that the distances R_i remain unchanged (i. e., the slight influence on the zero-field splitting of the change of the distances R_i is not considered here). Thus, by fitting the calculated pressure and stress dependences of splitting D to the observed values, we obtain for Ni^{2+} in the X site

$$\begin{aligned} d\ln\beta/dP &\approx -2.97 \times 10^{-3}\,(\text{kbar})^{-1}, \\ d\ln\beta/dU &\approx 1.43 \times 10^{-3}\,(\text{kbar})^{-1} \end{aligned} \tag{7}$$

and for Ni^{2+} in the Y site

$$\begin{aligned} d\ln\beta_i/dP &\approx -1.19 \times 10^{-3}\,(\text{kbar})^{-1}, \\ d\ln\beta_i/dU &\approx 0.70 \times 10^{-3}\,(\text{kbar})^{-1}. \end{aligned} \tag{8}$$

Comparisons of the pressure and stress dependences of D between calculation and experiment are also shown in Table 1.

3. Discussions

From the above studies one finds that the local angles $\beta_i^!$ for the two Ni^{2+} centers in LMN are only slightly different from the corresponding host ones; while the local angular compressibilities under pressure and stress are quite different not only from the corresponding host ones, but also for the two centers in the same crystal. Considering that the impurity ion Ni^{2+} and the replaced host ion Mg^{2+} have the same valence and similar ionic radii ($r_{Ni^{2+}} \approx 0.69$ Å and $r_{Mg^{2+}} \approx 0.66$ Å [15]), the former difference (local angles β_i) can be understood, but the latter (local angular compressibilities) seems astonishing. It should be pointed out that, generally speaking, there are two cases where the local compressibililties differ from those in the bulk, i. e., (i) the size and/or charge of impurity are unlike those of the replaced host ion [16, 17], and (ii) the studied crystal has a complex composition and structure, so that even if the impurity is absent, the different bonds and groups (or polyhedra) in the same crystal change by different amounts with increasing pressure or stress because the interactive forces in different groups are not the same. This means that the local compressibilities of the different groups or polyhedra are quite different, while the usual compressibilitity represents only the average value for the whole (or bulk) crystal [18 - 20]. Since (i) the composition and structure of LMN is complex, (ii) the size and charge of the impurity ion Ni^{2+} are close to those of the replaced host ion Mg^{2+}, and (iii) the local angular compressibilities of the two Ni^{2+} centers in LMN are different not only from each other, but also from the corresponding host ones, we suggest that the second case (i. e., the local angular compressibilities for distinctive groups or octahedra in the pure LMN are quite unlike) is the main cause that results in the above local compressibilities for both Ni^{2+} centers in LMN crystal.

[1] M. R. Anderson, G. T. Jenkin, and J. W. White, Acta Cryst. **B33**, 3933 (1977).
[2] A. A. Galkin, S. N. Lukin, and G. A. Tsintsadze, Sov. J. Low Temp. Phys. **2**, 574 (1976).
[3] V. N. Vasyukov and S. N. Lukin, Sov. Phys. Solid State **27**, 1169 (1985).
[4] A. K. Petrosyan and A. A. Mirzakhanyan, Phys. Status Solidi **B133**, 315 (1986).

[5] D. J. Newman and B. Ng, Rep. Prog. Phys. **52**, 699 (1989).
[6] W. C. Zheng and S. Y. Wu, Z. Naturforsch. **55a**, 915 (2000).
[7] W. L. Yu, X. M. Zheng, L. X. Yang, and B. Q. Zen, Phys. Rev. **B50**, 6756 (1994).
[8] A. Edgar, J. Phys. C: Solid State Phys. **9**, 4304 (1976).
[9] J. D. Newman, D. C. Pryce, and W. A. Runciamn, Amer. Mineral. **63**, 1278 (1978).
[10] S. Ray, A. Zalkin, and D. H. Templeton, Acta Cryst. **B29**, 2741 (1973).
[11] M. H. L. Pryce, G. Agnetta, T. Gasofano, M. B. Palma-Vittorelli, and M. U. Palma, Philos. Mag. **10**, 477 (1964).
[12] M. G. Zhao, J. A. Xu, and G. R. Bai, Sci. Sin. **25**, 1066 (1982).
[13] J. S. Griffith, The Theory of Transition-Metal Ions, Cambridge University Press, London 1964.
[14] V. N. Uasyukov and S. N. Lukin, Sov. Phys. Solid State **27**, 640 (1985).
[15] R. C. Weast, CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton 1989, pF. 164.
[16] M. J. L. Sangster, J. Phys. C: Solid State Phys. **14**, 2889 (1981).
[17] W. C. Zheng, Physica **B222**, 243 (1996).
[18] R. M. Hazen, Phys. Chem. Minerals **14**, 13 (1987).
[19] W. C. Zheng, J. Phys.: Condens. Matter **7**, 8351 (1995).
[20] R. H. Hazen and L. W. Finger, Amer. Mineral. **63**, 297 (1978).