

Theoretical studies of the local structures and EPR parameters for Cu^{2+} center in $\text{Cd}_2(\text{NH}_4)_2(\text{SO}_4)_3$ single crystal

Ch.-Y. Li*, L.-B. Chen, J.-J. Mao, X.-M. Zheng

School of Physics and Electronic Information, Shangrao Normal University, Shangrao Jiangxi 334000, P. R. China

Received March 24, 2015, in final form July 10, 2015

The electron paramagnetic resonance (EPR) parameters (g factors g_i and the hyperfine structure constants A_i , $i = x, y, z$) are interpreted by using the perturbation formulae for a $3d^9$ ion in rhombically (D_{2h}) elongated octahedra. In the calculated formulae, the crystal field parameters are set up from the superposition model, and the contribution to the EPR parameters from the admixture of d -orbitals in the ground state wave function of the Cu^{2+} ion was taken into account. Based on the calculation, local structural parameters of the impurity Cu^{2+} center in $\text{Cd}_2(\text{NH}_4)_2(\text{SO}_4)_3$ (CAS) crystal were obtained (i.e., $R_x \approx 2.05 \text{ \AA}$, $R_y \approx 1.91 \text{ \AA}$, $R_z \approx 2.32 \text{ \AA}$). The theoretical EPR parameters based on the above $\text{Cu}^{2+}-\text{O}^{2-}$ bond lengths in CAS crystal show a good agreement with the observed values. The results are discussed.

Key words: defect structure, electron paramagnetic resonance, cadmium ammonium sulphate crystal, Cu^{2+} doping

PACS: 76.30.Fc, 75.10.Dg, 71.70.ch

1. Introduction

Single crystal $\text{Cd}_2(\text{NH}_4)_2(\text{SO}_4)_3$ (CAS) has attracted interest of researchers due to the unique dielectric [1], phase transition [2], optical [3], birefringent and electrooptical properties [4]. The above properties may be closely related to the local structures, chemical bonding and electronic states of the doped ions in the hosts. Electron paramagnetic resonance (EPR) has long been considered as one of the most useful tools for the experimental study of chemical bonding. The EPR method provides a detailed description of the ground state of paramagnetic ions and enables one to explain the nature of crystal field and its symmetry produced by ligands around the metal ion [5–7]. Among these transition metal ions, Cu^{2+} ions with $3d^9$ configuration are widely used as paramagnetic probes as they represent a relatively simple one-hole magnetic system which can be used to obtain information regarding the electron wave function when there is a ligand field of low symmetry. Thus, EPR spectra of Cu^{2+} ion in different diamagnetic host lattices have been studied by many workers to get some data on the structure, dynamics and environment of host lattices [8–12]. For example, the EPR experiments were carried out for Cu^{2+} doped in CAS single crystal, and the EPR parameters (anisotropic g factors g_i and the hyperfine structure constants A_i , $i = x, y, z$) were also measured for rhombic Cu^{2+} center [13]. However, no satisfactory interpretation to the above experimental results has been made so far, and the data on the defect structures of Cu^{2+} center have not been obtained yet.

Considering that (i) the data on local structures and electronic states for Cu^{2+} in the CAS single crystal would be helpful in understanding the microscopic mechanisms of EPR behaviors of this material containing Cu^{2+} dopants and (ii) the anisotropic g factors for a d^9 ion in crystals are sensitive to its immediate environment (and hence to defect structure of d^9 impurity center). Thus, further investigations on EPR parameters and the defect structures for the Cu^{2+} center are of fundamental and practical significance.

*E-mail: cyl1962@126.com

In this paper, we have carried out local structure calculations for a paramagnetic Cu^{2+} center in CAS and have interpreted the EPR parameters in this system. The theoretical results are in good agreement with the experimental values. The $\text{Cu}^{2+}-\text{O}^{2-}$ bond lengths are obtained as follows: $R_x \approx 2.05 \text{ \AA}$, $R_y \approx 1.91 \text{ \AA}$, $R_z \approx 2.32 \text{ \AA}$.

2. Calculation

In the lattice of CAS crystal, each Cd^{2+} is surrounded by six oxygen atoms which form a slightly distorted octahedron [13]. When Cu^{2+} is doped in CAS crystal, it enters the lattice at Cd^{2+} site. For a $3d^9$ (Cu^{2+}) ion in an octahedral complex with a rhombic elongation it would give $g_z > g_x$, $g_y > 2$ [12, 14, 15]. Experimental results of EPR parameters in reference [9] agree with this relation. That is to say, the studied $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ clusters in CAS crystal are in rhombically elongated octahedra. However, the host $\text{Cd}(\text{H}_2\text{O})_6^{2+}$ clusters in CAS crystal are under rhombically compressed octahedra similar to many other tutton [16]. A Jahn-Teller ion is due to Cu^{2+} . When it occupies a cubic or trigonal octahedral site, the ground state is doublet 2E . The degeneracy of 2E state should be removed by Jahn-Teller effect, which makes these octahedral CuL_6 clusters become rhombic. Thus, the change of compressed $\text{Cd}(\text{H}_2\text{O})_6^{2+}$ octahedra in the host crystals to elongated $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ octahedra in the impurity centers due to Jahn-Teller effect for Cu^{2+} doped CAS crystal becomes understandable.

The local structures of the impurity Cu^{2+} center in CAS single crystal under rhombic symmetry are described by the metal-ligand distance R_i ($i = x, y, z$). Then, from the superposition model [17] and local geometrical relationship of the impurity Cu^{2+} center, the rhombic field parameters D_s , D_t , D_ξ and D_η can be expressed as follows:

$$\begin{aligned} D_s &= \frac{4}{7} \bar{A}_2(R_0) \left[\left(\frac{R_0}{R_x} \right)^{t_2} + \left(\frac{R_0}{R_y} \right)^{t_2} - 2 \left(\frac{R_0}{R_z} \right)^{t_2} \right], \\ D_t &= \frac{8}{21} \bar{A}_4(R_0) \left[\left(\frac{R_0}{R_x} \right)^{t_4} + \left(\frac{R_0}{R_y} \right)^{t_4} - 2 \left(\frac{R_0}{R_z} \right)^{t_4} \right], \\ D_\xi &= \frac{2}{7} \bar{A}_2(R_0) \left[\left(\frac{R_0}{R_x} \right)^{t_2} - \left(\frac{R_0}{R_y} \right)^{t_2} \right], \\ D_\eta &= \frac{10}{21} \bar{A}_4(R_0) \left[\left(\frac{R_0}{R_x} \right)^{t_4} - \left(\frac{R_0}{R_y} \right)^{t_4} \right]. \end{aligned} \quad (1)$$

Here, $t_2 \approx 3$ and $t_4 \approx 5$ are the power-law exponents due to the dominant ionic nature of the bonds [9, 12, 18–20]. $\bar{A}_2(R_0)$, and $\bar{A}_4(R_0)$ are intrinsic parameters with the reference distance R_0 [taken as $R_0 = \bar{R} = (R_x + R_y + R_z)/3$]. The ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0)$ was found to be in the range 9–12 as per several studies of optical and EPR spectra using superposition model for $3d^n$ ions in crystals [12, 19–22]. Here, we take $\bar{A}_2(R_0)/\bar{A}_4(R_0) = 12$. Therefore, axial and perpendicular anisotropies $\Delta g [= g_z - (g_x + g_y)/2]$ and $\delta g [= g_y - g_x]$ of EPR g factors are correlated to the rhombic field parameters and hence to the local structures of the systems studied.

For a $3d^9$ (Cu^{2+}) ion under rhombically elongated octahedra, its lower orbital doublet 2E_g would be separated into two singlets ${}^2A_{1g}(\theta)$ and ${}^2A_{1g}(\epsilon)$. Meanwhile, the higher cubic orbital triplet ${}^2T_{2g}$ would be split into three singlets ${}^2B_{1g}(\zeta)$, ${}^2B_{2g}(\eta)$ and ${}^2B_{3g}(\xi)$ [9]. Since the states ${}^2A_{1g}(\theta)$ and ${}^2A_{1g}(\epsilon)$ belong to the same representation of rhombic symmetry group, the ground state will be neither ${}^2A_{1g}(\theta)$ nor ${}^2A_{1g}(\epsilon)$ but an admixture of both [8, 22], i.e.,

$$\Phi = N \left[\alpha |d_{x^2-y^2}\rangle + \beta |d_{3z^2-r^2}\rangle \right], \quad (2)$$

where N is the probability of finding electron in the metal d -orbital, the characteristic of covalency of the system. α and β are the mixing coefficients due to the rhombic field components and satisfy the normalization relation:

$$\alpha^2 + \beta^2 = 1. \quad (3)$$

From perturbation theory, the high-order perturbation formulae of EPR parameters (g factors g_x , g_y , g_z and hyperfine structure constants A_x , A_y , A_z) for $3d^9$ ions in rhombic symmetry can be expressed as [14, 22]:

$$\begin{aligned}
g_x &= g_s + \frac{2k\zeta(\alpha + \sqrt{3}\beta)}{E_4} - \frac{2\alpha k\zeta^2(\alpha + \sqrt{3}\beta)}{E_2E_4} + \frac{k\zeta^2(\alpha^2 - 3\beta^2)}{E_3E_4} \\
&\quad - \frac{2\alpha^2 g_s \zeta^2}{E_2^2} - \frac{g_s \zeta^2(\alpha - \sqrt{3}\beta)^2}{2E_3^2} + \frac{2\alpha k\zeta^2(\alpha - \sqrt{3}\beta)^2}{E_2E_3}, \\
g_y &= g_s + \frac{2k\zeta(\alpha - \sqrt{3}\beta)}{E_3} - \frac{2\alpha k\zeta^2(\alpha - \sqrt{3}\beta)}{E_2E_3} + \frac{k\zeta^2(\alpha^2 - 3\beta^2)}{E_3E_4} \\
&\quad - \frac{2\alpha^2 g_s \zeta^2}{E_2^2} - \frac{g_s \zeta^2(\alpha + \sqrt{3}\beta)^2}{2E_4^2} + \frac{2\alpha k\zeta^2(\alpha + \sqrt{3}\beta)^2}{E_2E_4}, \\
g_z &= g_s + \frac{8\alpha^2 k\zeta}{E_2} - \frac{2\alpha k\zeta^2(\alpha - \sqrt{3}\beta)}{E_2E_3} - \frac{2\alpha k\zeta^2(\alpha + \sqrt{3}\beta)}{E_2E_4} \\
&\quad - \frac{g_s \zeta^2(\alpha - \sqrt{3}\beta)}{2E_3^2} - \frac{g_s \zeta^2(\alpha + \sqrt{3}\beta)^2}{2E_4^2} - \frac{k\zeta^2(\alpha - 3\beta^2)}{E_3E_4},
\end{aligned} \tag{4}$$

$$\begin{aligned}
A_x &= P_0 \left[-\kappa + \frac{2N^2}{7} - \kappa' + (g_x - g_s) - \frac{3}{14}(g_y - g_s) \right], \\
A_y &= P_0 \left[-\kappa + \frac{2N^2}{7} + \kappa' + (g_y - g_s) - \frac{3}{14}(g_x - g_s) \right], \\
A_z &= P_0 \left[-\kappa - \frac{4N^2}{7} + (g_z - g_s) + \frac{3}{14}(g_x + g_y - 2g_s) \right].
\end{aligned} \tag{5}$$

Here, g_s (≈ 2.0023) is the spin-only value. k ($\approx N$) is the orbital reduction factor. P_0 ($\approx 172 \times 10^{-4} \text{ cm}^{-1}$ [23, 24]) is the dipolar hyperfine interaction parameter. The spin-orbit coupling coefficient for CAS:Cu²⁺ is acquired as the free-ion value ζ_0 ($\approx 829 \text{ cm}^{-1}$ [25]) multiplying N . κ and κ' are the isotropic and anisotropic core polarization constants, respectively. The denominators E_i ($i = 1 - 4$) can be obtained from the energy matrices for a $3d^9$ ion under rhombic symmetry in terms of the cubic field parameter D_q and the rhombic field parameters D_s , D_t , D_ξ and D_η :

$$\begin{aligned}
E_1 &= 4D_s + 5D_t, \\
E_2 &= 10D_q, \\
E_3 &= 10D_q + 3D_s - 5D_t - 3D_\xi + 4D_\eta, \\
E_4 &= 10D_q + 3D_s - 5D_t + 3D_\xi - 4D_\eta.
\end{aligned} \tag{6}$$

According to optical spectral studies for Cu²⁺ in oxides with similar [CuO₆]¹⁰⁻ cluster [26, 27], the cubic field parameter D_q ($\approx 1050 \text{ cm}^{-1}$) and the orbital reduction factor k (≈ 0.84) can be obtained. From the core polarization constant κ ($\approx 0.2 - 0.6$ [8, 9, 20, 24]) for Cu²⁺ in many crystals with similar [CuO₆]¹⁰⁻ clusters, one can estimate κ (≈ 0.34) for the system studied here. In view of the anisotropic contributions to hyperfine structure constants from Cu²⁺ $3d-3s$ ($4s$) orbital admixtures, the anisotropic core polarization constants are taken as κ' (≈ 0.021).

Then, for the impurity Cu²⁺ in CAS single crystal, we take the Cu²⁺-O²⁻ bond lengths:

$$R_x \approx 2.05 \text{ \AA}, \quad R_y \approx 1.91 \text{ \AA} \quad \text{and} \quad R_z \approx 2.32 \text{ \AA}. \tag{7}$$

Substituting the above values into the matrix formulae in equation (1), and using the ground state wave function as follows:

$$\Phi = 0.85 \left[0.995|d_{x^2-y^2} + 0.0999|d_{3z^2-r^2} \right] \tag{8}$$

the calculated results (Cal^b.) of EPR parameters are shown in table 1. For comparison, the results (Cal^a.) based on the omission of admixture ²A_{1g}(θ) and ²A_{1g}(ϵ) states (i.e., taking $\alpha = 1$, $\beta = 0$) are also listed in table 1.

Table 1. The calculated and experimental anisotropic g factors and hyperfine structure constants (in 10^{-4} cm^{-1}) for Cu^{2+} in $\text{Cd}_2(\text{NH}_4)_2(\text{SO}_4)_3$ single crystal.

	g_x	g_y	g_z	A_x	A_y	A_z
Cal ^a .	2.078	2.047	2.431	-33.5	-32.0	-103.8
Cal ^b .	2.145	2.096	2.412	-19.7	-13.1	-101.9
Expt.[9]	2.144	2.094	2.415	18.7	15.9	97.1

^a Calculations based on the perturbation formulae but with the omission of admixture ${}^2A_{1g}(\theta)$ and ${}^2A_{1g}(\epsilon)$ states (i.e., taking $\alpha = 1, \beta = 0$).

^b Calculations based on the perturbation formulae and considering the admixture of ${}^2A_{1g}(\theta)$ and ${}^2A_{1g}(\epsilon)$ states.

3. Discussion

From table 1, it can be seen that the calculated EPR parameters are in good agreement with the experimental data. Thus, the obtained $\text{Cu}^{2+}-\text{O}^{2-}$ bond lengths and admixture coefficients of d -orbitals for the impurity Cu^{2+} ion in CAS single crystal are reasonable.

1. From table 1, one can find that the calculated EPR parameters by using the perturbation formulae and considering the admixture of the ground states ${}^2A_{1g}(\theta)$ and ${}^2A_{1g}(\epsilon)$ are in good agreement with the experimental data and the results are better than those obtained using the above formulas while neglecting the admixture of the d -orbitals (i.e., $\alpha = 1, \beta = 0$). Moreover, it is noted that the mixing coefficient α (≈ 0.980) is very close to that ($\alpha \approx 0.977 - 0.996$ [8, 14, 22]) based on the analysis of EPR parameters for similar rhombic Cu^{2+} centers in many crystals.

2. From table 1, one can see that the absolute values of the calculated hyperfine structure constants A_i are in good agreement with the experimental findings, but the signs of all of them are negative. Actually, the signs of hyperfine structure constants are very difficult to ascertain. Thus, many experiments give them as absolute ones [8, 24, 28, 29]. However, negative signs of constants A_i for $3d^n$ ions in many crystals were proposed [20–23]. Thus, the negative signs of hyperfine structure constants obtained in this work can be regarded as reasonable.

4. Conclusion

The EPR parameters and the local structures of rhombic Cu^{2+} center in the CAS crystal are theoretically investigated from perturbation formulae for a $3d^9$ ion in rhombically elongated octahedra. The theoretical results based on the above perturbation formulae and considering the admixture of the ground states ${}^2A_{1g}(\theta)$ and ${}^2A_{1g}(\epsilon)$ are in good agreement with the experimental data. The ligand octahedra around Cu^{2+} are found to suffer a relative elongation along the C_4 axis due to Jahn-Teller effect, which may entirely depress the original compressed $\text{Cd}(\text{H}_2\text{O})_6^{2+}$ octahedra in the host crystals.

Acknowledgements

This work was financially supported by Chinese Natural Science Foundation (grants 11365017, 11465015).

References

1. Glogarová M., Fousek J., Phys. Status Solidi A, 1973, **15**, 579; doi:10.1002/pssa.2210150227.
2. Kreske S., Devarajan V., J. Phys. C: Solid State Phys., 1982, **15**, 7333; doi:10.1088/0022-3719/15/36/015.
3. Satyanarayana N., Radhakrishna S., Solid State Commun., 1985, **54**, 891; doi:10.1016/0038-1098(85)91164-0.
4. Konak C., Fousek J., Ivanov N.R., Ferroelectrics, 1973, **6**, 235; doi:10.1080/00150197408243973.
5. Kripal R., Misra M.G., Dwivedi P., Appl. Magn. Reson., 2012, **42**, 251; doi:10.1007/s00723-011-0286-5.
6. Swalen J.D., Johnson B., Gladney H.M., J. Chem. Phys., 1970, **52**, 4078; doi:10.1063/1.1673613.
7. Bozkurt E., Karabulut B., Kartal İ., Spectrochim. Acta A, 2009, **73**, 163; doi:10.1016/j.saa.2009.02.015.
8. Kartal İ., Karabulut B., Köksal F., İçbudak H., Z. Naturforsch. A, 2000, **55**, 887; doi:10.1515/zna-2000-11-1208.
9. Kuang M.Q., Wu S.Y., Zhang H.M., Optik, 2012, **123**, 1601; doi:10.1016/j.ijleo.2011.08.032.
10. Aramburu J.A., Moreno M., J. Chem. Phys., 1985, **83**, 6071; doi:10.1063/1.449597.
11. Abragam A., Bleaney B., Electron Paramagnetic Resonance of Transition Ions, Oxford University Press, London, 1970.
12. Zhang H.M., Wu S.Y., Kuang M.Q., Zhang Z.H., J. Phys. Chem. Solids, 2012, **73**, 846; doi:10.1016/j.jpss.2012.02.021.
13. Yerima J.B., Dikko A.B., De D.K., The IJES, 2014, **3**, No. 7, 48.
14. Zhang D.T., He L., Yang W.Q., Zheng W.C., Physica B, 2010, **405**, 3642; doi:10.1016/j.physb.2010.05.057.
15. Dong H.N., Wu S.Y., Li P., Phys. Status Solidi B, 2004, **241**, 1935; doi:10.1002/pssb.200402033.
16. Petrashen V.E., Yablokov Yu.V., Davidovich R.L., Phys. Status Solidi B, 1980, **101**, 117; doi:10.1002/pssb.2221010112.
17. Newman D.J., Ng B., Rep. Prog. Phys., 1989, **52**, 699; doi:10.1088/0034-4885/52/6/002.
18. Wei W.H., Wu S.Y., Dong H.N., Z. Naturforsch. A, 2005, **60**, 541; doi:10.1515/zna-2005-0713.
19. Rudowicz C., Yang Z.Y., Yueng Y.Y., Qin J., J. Phys. Chem. Solids, 2003, **64**, 1419; doi:10.1016/S0022-3697(03)00190-2.
20. Zhang H.M., Wan X., Zhang Z.M., Z. Naturforsch. A, 2012, **67**, 407; doi:10.5560/zna.2012-0030.
21. Dong H.N., Wu S.Y., Liu X.R., Chen W.D., Z. Naturforsch. A, 2005, **60**, 373; doi:10.1515/zna-2005-0509.
22. Zhang H.M., Xiao W.B., Wan X., Radiat. Eff. Defects Solids, 2014, **169**, 603; doi:10.1080/10420150.2014.913590.
23. Dong H.N., Wu S.Y., Li P., Phys. Status Solidi B, 2004, **241**, 1935; doi:10.1002/pssb.200402033.
24. McGarvey B.R., J. Chem. Phys., 1967, **71**, 51; doi:10.1021/j100860a007.
25. Griffith J.S., The Theory of Transition-Metal Ions, Cambridge University Press, London, 1964.
26. Chakravarty A.S., Introduction to the Magnetic Properties of Solids, Wiley Interscience Publication, New York, 1980.
27. Jorgensen C.K., Absorption Spectra and Chemical Bonding in Complexes, 2nd Edn., Pergamon Press, Oxford, 1964.
28. Kripal R., Singh D.K., Spectrochim. Acta A, 2007, **67**, 815; doi:10.1016/j.saa.2006.08.038.
29. Kalfaoglu E., Karabulut B., Chem. Phys. Lett., 2011, **505**, 154; doi:10.1016/j.cplett.2011.02.038.

Теоретичні дослідження локальних структур та параметрів електронного парамагнітного резонансу для центру Cu²⁺ в монокристалі Cd₂(NH₄)₂(SO₄)₃

Ч.-І. Лі, Л.Б. Чен, Дж.-Дж. Мао, Кс.-М. Женг

Школа фізики і електронної інформації, Нормальний університет Шанграо, Шанграо Цзянсі, КНР

Параметри електронного парамагнітного резонансу (ЕПР) (g -фактори g_i і константи надтонкої структури A_i , $i = x, y, z$) інтерпретуються за допомогою формули збурень для іона $3d^9$ у ромбічно (D_{2h}) видовженому восьмиграннику. У формулах параметри кристалічного поля встановлюються згідно суперпозиційної моделі, де враховується внесок у параметри ЕПР від домішування d -орбіталей в основному стані хвильової функції Cu^{2+} . На основі обчислень отримано локальні структурні параметри домішки центру Cu^{2+} у кристалі $Cd_2(NH_4)_2(SO_4)_3$ (CAS) (тобто, $R_x \approx 2.05 \text{ \AA}$, $R_y \approx 1.91 \text{ \AA}$, $R_z \approx 2.32 \text{ \AA}$). Теоретичні параметри ЕПР, що базуються на вищезгаданих довжинах $Cu^{2+}-O^{2-}$ зв'язку у CAS кристалі, демонструють хороше узгодження з спостережуваними значеннями. Результати досліджень обговорюються.

Ключові слова: дефектна структура, електронний парамагнітний резонанс, кристал кадмій амонієвого сульфату, легування Cu^{2+}
