

Theoretical Investigations of the Spin Hamiltonian Parameters and the Local Structure of a Trigonal Co^{2+} Center in $\text{Bi}_4\text{Ge}_3\text{O}_{12}$

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The spin Hamiltonian parameters anisotropic g factors g_{\parallel} , g_{\perp} and hyperfine structure constants A_{\parallel} and A_{\perp} , as well as the local structure of the trigonal Co^{2+} center in $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) are theoretically investigated by the perturbation formulas of the spin Hamiltonian parameters for a $3d^7$ ion in trigonal symmetry, based on the cluster approach. It is found that the impurity Co^{2+} substituting the host Bi^{3+} undergoes an off-center displacement ΔZ ($\approx -0.132 \text{ \AA}$) away from the center of the oxygen octahedron along the C_3 axis. The spin Hamiltonian parameters based on the above displacement show reasonable agreement with the observed values. The results are discussed.

Key words: Electron Paramagnetic Resonance (EPR); Crystal-field Theory and Spin Hamiltonians; Defect Structure; Co^{2+} ; $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO).

1. Introduction

Single crystals of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO, i. e., the 2:3 stoichiometry of bismuth germinates) have extensively investigated due to their practical applications as scintillators for the detection of high-energy photons and particles [1, 2], promising potential as nonlinear optical devices [3, 4] and solid-state laser hosts [5] as well as holographic gratings in pure crystals and transition-metal (e. g., Cr, Co, Fe and Mn) doped materials [6–8]. The above properties and applications of BGO are sensitively related to the presence of impurities [9]. For example, as regards optoelectronic applications, transition-metal-doped samples have been found to exhibit both photochromic and photorefractive effects [6–9]. To study its impurity behaviour, EPR experiments have been carried out on cobalt doped BGO, and the spin Hamiltonian parameters g factors g_{\parallel} , g_{\perp} and the hyperfine structure constants A_{\parallel} and A_{\perp} were measured for the trigonal Co^{2+} impurity center [10]. Although the above EPR signals were attributed to the impurity Co^{2+} occupying the trigonally-distorted octahedral Bi^{3+} site [10], the spin Hamiltonian parameters have not been theoretically interpreted, and

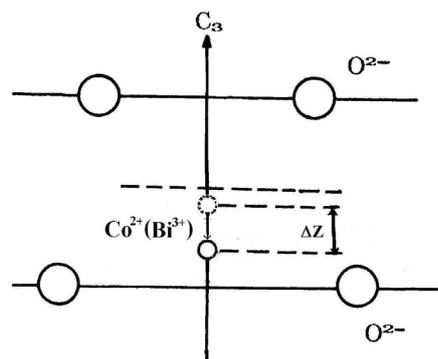


Fig. 1. Local structure of the trigonal Co^{2+} center in BGO. The impurity Co^{2+} replacing the host Bi^{3+} ion undergoes an off-center displacement ΔZ away from the center of the oxygen octahedron along the C_3 axis.

the local structure for this center has not been determined either. In order to make further investigations on the spin Hamiltonian parameters and the local structure of the trigonal Co^{2+} center in BGO, in this paper, we study these parameters and the local structure of this center from the perturbation formulas of the spin Hamiltonian parameters for a $3d^7$ ion in trigonal symmetry.

2. Calculations

For a $\text{Co}^{2+}(3d^7)$ ion in trigonally distorted octahedra, the second-order perturbation formulas of the spin Hamiltonian parameters g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} , based on the cluster approach, can be expressed as [11]

$$\begin{aligned}
 g_{\parallel} &= 2 + \frac{4(k\alpha + 2) \left[\frac{3}{x^2} - \frac{4}{(x+2)^2} \right] + 2 \left[\frac{9}{x^2} - \frac{4}{(x+2)^2} \right] v_1 + \left(\frac{\alpha}{\alpha'} \right)^2 v_2 - 2 \left(\frac{\alpha}{\alpha'} \right) \left[\frac{3}{x} - \frac{4}{x+2} \right] v_3}{\left[\left(\frac{\alpha}{\alpha'} \right)^2 + \frac{6}{x^2} + \frac{8}{(x+2)^2} \right]}, \\
 g_{\perp} &= \frac{4 \left[\left(\frac{\alpha}{\alpha'} \right)^2 + \frac{2k\alpha}{x+2} + \frac{12}{x(x+2)} \right] + \left(\frac{\alpha}{\alpha'} \right)^2 v_4 + \frac{8}{(x+2)^2} v_5 + \frac{12}{x(x+2)} v_6 - \left(\frac{\alpha}{\alpha'} \right) \frac{4}{(x+2)} v_7}{\left[\left(\frac{\alpha}{\alpha'} \right)^2 + \frac{6}{x^2} + \frac{8}{(x+2)^2} \right]}, \\
 A_{\parallel} &= P \left\{ (-\kappa/2) \left[2 + \frac{8 \left[\frac{3}{x^2} - \frac{4}{(x+2)^2} \right]}{\left[\left(\frac{\alpha}{\alpha'} \right)^2 + \frac{6}{x^2} + \frac{8}{(x+2)^2} \right]} \right] + \frac{4k\alpha \left[\frac{3}{x^2} - \frac{4}{(x+2)^2} \right]}{\left[\left(\frac{\alpha}{\alpha'} \right)^2 + \frac{6}{x^2} + \frac{8}{(x+2)^2} \right]} \right\} \\
 &\quad + P' \frac{2 \left[\frac{9}{x^2} - \frac{4}{(x+2)^2} \right] W_x + \left(\frac{\alpha}{\alpha'} \right)^2 W_z - 4 \left(\frac{\alpha}{\alpha'} \right) \left[\frac{3}{x} - \frac{4}{x+2} \right] W_{xz}}{\left[\left(\frac{\alpha}{\alpha'} \right)^2 + \frac{6}{x^2} + \frac{8}{(x+2)^2} \right]}, \\
 A_{\perp} &= P \frac{-2\kappa \left[\left(\frac{\alpha}{\alpha'} \right)^2 + \frac{12}{x(x+2)} \right] + \frac{8k\alpha}{x+2}}{\left[\left(\frac{\alpha}{\alpha'} \right)^2 + \frac{6}{x^2} + \frac{8}{(x+2)^2} \right]} + P' \frac{-\frac{12}{x(x+2)} W_x - \left(\frac{\alpha}{\alpha'} \right)^2 W_z - \frac{32}{(x+2)^2} W_{xy} + \left(\frac{\alpha}{\alpha'} \right) \frac{4}{(x+2)} W_{xz}}{\left[\left(\frac{\alpha}{\alpha'} \right)^2 + \frac{6}{x^2} + \frac{8}{(x+2)^2} \right]},
 \end{aligned} \tag{1}$$

where κ is the core polarization constant. x can be determined from the energy splitting $\Delta [= E(^4A_2) - E(^4E)]$ of the ground orbital state 4T_1 in trigonal crystal-fields by using the relationship $\Delta = \frac{\zeta\alpha'^2}{3\alpha} \left[\frac{3}{x} + \frac{4}{x+2} \right] - \frac{\zeta\alpha}{6}(x+3)$ [11]. The splitting Δ can be obtained from the d-d transition energy matrices for a $3d^7$ ion in trigonal symmetry.

The parameters α , α' , v_i and W_{ij} in (1) are related to the admixture among the ground and excited states via crystal-field and electrostatic interactions (note: their detailed expressions can be found in [11]). Since the trigonal field parameters V and V' occur in these expressions and the energy matrices, the anisotropies $\Delta g (= g_{\parallel} - g_{\perp})$ and $\Delta A (= A_{\parallel} - A_{\perp})$ for the g and A factors are related to the trigonal field parameters and hence to the trigonal distortion (or local structure) of the studied Co^{2+} impurity center.

Based on the cluster approach, the orbital reduction factors k and k' , the spin-orbit coupling coefficients

ζ and ζ' , and the dipolar hyperfine structure parameters P and P' can be determined by using the expressions [11]

$$\begin{aligned}
 k &= N_t(1 + \lambda_t^2/2), \quad k' = (N_t N_e)^{1/2}(1 - \lambda_t \lambda_e/2), \\
 \zeta &= N_t(\zeta_d^0 + \lambda_t^2 \zeta_p^0/2), \\
 \zeta' &= (N_t N_e)^{1/2}(\zeta_d^0 - \lambda_t \lambda_e \zeta_p^0/2), \\
 P &= N_t P_0, \quad P' = (N_t N_e)^{1/2} P_0,
 \end{aligned} \tag{2}$$

where ζ_d^0 or ζ_p^0 is the spin-orbit coupling coefficient of the d electrons for a $3d^7$ ion or that of the p electrons for a ligand ion in free state. P_0 is the dipolar hyperfine structure parameter for a free $3d^7$ ion. N_{γ} ($\gamma = e_g$ or t_{2g}) is the normalization factor and λ_{γ} is the orbital mixing coefficient. By the semiempirical LCAO method [11, 12], these parameters can be obtained from the normalization condition

$$N_{\gamma}(1 - 2\lambda_{\gamma} S_{dp}(\gamma) + \lambda_{\gamma}^2) = 1 \tag{3}$$

Table 1. The spin Hamiltonian parameters g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} for the trigonal Co^{2+} center in BGO.

	g_{\parallel}	g_{\perp}	Δg	A_{\parallel} (10^{-4} cm^{-1}) ^c	A_{\perp} (10^{-4} cm^{-1}) ^c	ΔA (10^{-4} cm^{-1})
Calc. ^a	3.174	5.021	-1.847	6.3	187.9	-181.6
Calc. ^b	2.813	5.175	-2.362	-8.6	195.0	-203.6
Expt. [10]	2.765 (5)	5.160 (1)	-2.395(6)	~ 10	196.6 (2)	-196.6(102)

^a Calculations based on the impurity Co^{2+} at the ideal Bi^{3+} site, i. e., $\Delta Z = 0$. ^b Calculations based on the local structural parameters in (9) due to the displacement ΔZ . ^c The signs of A_{\parallel} and A_{\perp} were not given in [10]. According to the studies in this work, we suggest that A_{\parallel} is negative and A_{\perp} is positive.

and the approximate relation [11, 12]

$$f_{\gamma} = N_{\gamma}^2 [1 + \lambda_{\gamma}^2 S_{\text{dp}}^2(\gamma) - 2\lambda_{\gamma} S_{\text{dp}}(\gamma)], \quad (4)$$

where $f_{\gamma} [\approx (B/B_0 + C/C_0)/2]$ is the ratio of the Racah parameters for a $3d^7$ ion in the crystal to those of the free ion. $S_{\text{dp}}(\gamma)$ are the group overlap integrals.

$$\begin{aligned} V &= (9/7)\bar{A}_2(R) \sum_i (R/R_i)^{t_2} (3 \cos^2 \beta_i - 1) \\ &\quad + \bar{A}_4(R) \sum_i (R/R_i)^{t_4} [(20/21)(35 \cos^4 \beta_i - 30 \cos^2 \beta_i + 3) + (20\sqrt{2}/3) \sin^3 \beta_i \cos \beta_i], \\ V' &= (-3\sqrt{2}/7)\bar{A}_2(R) \sum_i (R/R_i)^{t_2} (3 \cos^2 \beta_i - 1) \\ &\quad + \bar{A}_4(R) \sum_i (R/R_i)^{t_4} [(5\sqrt{2}/21)(35 \cos^4 \beta_i - 30 \cos^2 \beta_i + 3) + (10/3) \sin^3 \beta_i \cos \beta_i], \end{aligned} \quad (5)$$

where t_2 and t_4 are the power-law exponents. One can take $t_2 \approx 3$ and $t_4 \approx 5$ due to the ionic nature of the bonds [15, 16]. $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parameters with the reference bonding length R . For $3d^n$ ions in octahedra, $\bar{A}_4(R) \approx (3/4)D_q$ [15, 16] and $\bar{A}_2(R) \approx 10.8\bar{A}_4(R)$ [16, 17]. For the Bi^{3+} site in BGO, the host metal-ligand bonding lengths R_j^0 and the angles β_j^0 between R_j^0 and the C_3 axis are $R_1^0 \approx 2.149 \text{ \AA}$, $\beta_1^0 \approx 51.38^\circ$, $R_2^0 \approx 2.620 \text{ \AA}$, $\beta_2^0 \approx 104.62^\circ$ [18–20]. Usually, the impurity-ligand distances R_j may be unlike the host metal-ligand distances R_j^0 in pure BGO due to the difference of ionic radii between the impurity Co^{2+} and the replaced Bi^{3+} . However, we can estimate the distances R_j from the empirical relationship [21, 22]

$$R_j \approx R_j^{\text{H}} + (r_i - r_h)/2. \quad (6)$$

Thus, from the ionic radius r_i ($\approx 0.72 \text{ \AA}$ [23]) of Co^{2+} and the radius r_h ($\approx 0.95 \text{ \AA}$ [23]) of Bi^{3+} , the distances R_j are obtained. Here, the average \bar{R} ($\approx 2.270 \text{ \AA}$) is taken as the reference distance in (5), i. e., $R = \bar{R}$. By using the distance R and the Slater-type SCF functions

Strictly speaking, the structure around the host Bi^{3+} site in BGO has C_3 point symmetry. For simplicity, however, one can take the C_{3v} approach, as is done in many crystal-field and spin Hamiltonian calculations for paramagnetic ions in corundum-type crystals [13, 14]. With the superposition model (SPM) [15] and the local geometrical relationship of the $[\text{CoO}_6]^{10-}$ cluster in BGO: Co^{2+} (see Fig. 1), the trigonal field parameters V and V' can be expressed as

[24, 25], the group overlap integrals $S_{\text{dp}}(e_g) \approx 0.012$ and $S_{\text{dp}}(t_{2g}) \approx 0.003$ can be calculated.

For the BGO: Co^{2+} crystal, to our knowledge no optical spectral data were reported. However, one can deduce its spectral parameters from the optical spectra for similar trigonal $[\text{CoO}_6]^{10-}$ clusters in oxides (e. g., LiNbO_3 , $\alpha\text{-LiIO}_3$ [26]). Thus, we approximately have

$$\begin{aligned} B &\approx 810 \text{ cm}^{-1}, \quad C \approx 3780 \text{ cm}^{-1}, \\ D_q &\approx -660 \text{ cm}^{-1} \end{aligned} \quad (7)$$

for the studied system. For a free Co^{2+} ion [27], $B_0 \approx 1115 \text{ cm}^{-1}$ and $C_0 \approx 4366 \text{ cm}^{-1}$, thus $f_{\gamma} \approx 0.80$. From (3) and (4), we have $N_t \approx 0.893$, $N_e \approx 0.896$, $\lambda_t \approx 0.349$, $\lambda_e \approx 0.353$. Substituting the free-ion values $\zeta_d^0 \approx 533 \text{ cm}^{-1}$ [27], $P_0 \approx 254 \cdot 10^{-4} \text{ cm}^{-1}$ [28] of Co^{2+} and $\zeta_p^0 \approx 151 \text{ cm}^{-1}$ [29] of O^{2-} into (2), the parameters $k \approx 0.948$, $k' \approx 0.840$, $\zeta \approx 484 \text{ cm}^{-1}$, $\zeta' \approx 469 \text{ cm}^{-1}$, $P \approx 226 \cdot 10^{-4} \text{ cm}^{-1}$ and $P' \approx 227 \cdot 10^{-4} \text{ cm}^{-1}$ are calculated.

Substituting these parameters (including the trigonal field parameters V and V' based on the impurity Co^{2+} at the ideal Bi^{3+} site) and the core polarization constant

$\kappa \approx 0.325$ for Co^{2+} in oxides [11,30], the theoretical g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} for Co^{2+} in BGO are calculated and shown in Table 1.

From Table 1 it can be found that the calculated g and A factors based on the above structural data are inconsistent with the experimental data, particularly the anisotropies Δg and ΔA are smaller than the observed ones. This means that the estimated trigonal distortion based on the Co^{2+} ion at the exact Bi^{3+} site is somewhat smaller. As pointed out by the studies on impurity ions in trigonally-distorted octahedral environments [21,31], when the host cation is replaced by the impurity with different size and charge, it can be expected that the impurity ion does not occupy exactly the host site, but is shifted along the C_3 axis by an amount ΔZ . Therefore, Co^{2+} may undergo an off-center displacement ΔZ away from the center of the oxygen octahedron along the C_3 axis (see Fig. 1) so as to increase the trigonal distortion and hence the theoretical Δg and ΔA . Thus the new local structural parameters R'_j and β'_j can be determined from the ΔZ . By fitting the calculated Δg or ΔA to the experiment, one can obtain the displacement (note: the displacement direction towards the center of the oxygen octahedron is defined as positive)

$$\Delta Z \approx -0.132 \text{ \AA} \quad (8)$$

for the studied impurity center. The local structural parameters, based on the ΔZ are

$$\begin{aligned} R_1 &\approx 2.119 \text{ \AA}, & \beta_1 &\approx 48.59^\circ, \\ R_2 &\approx 2.475 \text{ \AA}, & \beta_2 &\approx 101.66^\circ. \end{aligned} \quad (9)$$

The corresponding spin Hamiltonian parameters are also collected in Table 1.

3. Discussions

Table 1 shows that the theoretical spin Hamiltonian parameters, especially the anisotropies Δg and ΔA based on the off-center displacement ΔZ , agree better with the experimental data than those based on Co^{2+} occupying the ideal Bi^{3+} site (i. e., $\Delta Z = 0$).

1. The local structural parameters in (9) for Co^{2+} in BGO indicate that the trigonal distortion is increased due to the outward displacement ΔZ of Co^{2+} , and then the $[\text{CoO}_6]^{10-}$ cluster is further compressed along the C_3 axis. Since the impurity Co^{2+} is smaller than the replaced Bi^{3+} , the immediate environment around the impurity may become looser. Meanwhile, the smaller

charge of Co^{2+} leads to a weaker electrostatic interaction acting upon the impurity than on the host. As a result, the impurity Co^{2+} may be unstable at the ideal Bi^{3+} site and then suffer the off-center displacement ΔZ away from the center of the oxygen octahedron. Interestingly, if one neglects ΔZ in the above calculations, good agreement between theory and experiment is difficult to achieve by modifying the ratio $\bar{A}_2(R)/\bar{A}_4(R)$ within the widely accepted range of $9 \sim 12$ [16] and even the values of the spectral parameters in (7). So, the displacement ΔZ obtained in this work can be regarded as suitable. Nevertheless, the structural parameters of Co^{2+} obtained in the present work are different from those ($R_1 \approx 2.10(5) \text{ \AA}$, $\beta_1 \approx 55(5)^\circ$, $R_2 \approx 2.2(1) \text{ \AA}$ and $\beta_2 \approx 125(9)^\circ$) of Mn^{2+} at the same Bi^{3+} site in BGO based on SPM analyses [32]. The local structure of the latter exhibits an almost regular $[\text{MnO}_6]^{10-}$ octahedron due to the shift of Mn^{2+} towards the center of the octahedron along the C_3 axis [32]. The above discrepancy seems to be attributed to different physical or chemical properties and hence different local behaviour of the two divalent ions in BGO. This point is worthy of further investigations.

2. It is noted that charge mismatching substitution of Bi^{3+} by Co^{2+} would possibly induce charge compensation around the impurity. Judging from the trigonal symmetry of the observed defect center, the probable means of compensation may be a Bi^{3+} in the neighbourhood of the central Co^{2+} substituted by a tetravalent diamagnetic impurity ion. It is however more likely that the charge compensation is far enough from the studied Co^{2+} center and its influence can also be regarded as small and negligible, as pointed out for similar divalent Mn^{2+} in oxides [32,33].

3. There may be some errors in the calculated spin Hamiltonian parameters and the displacement ΔZ due to the following: (i) Approximation of the theoretical model and related calculation formulas. (ii) In order to reduce the number of the adjustable parameters, displacements of the oxygen ligands were not included in the calculations. Little change would be induced by this effect. (iii) The errors of the SPM parameters may also have some influence on the final results. We find that the theoretical results are insensitive to the choice of $\bar{A}_2(R)$, when the ration $\bar{A}_2(R)/\bar{A}_4(R)$ changes within the range of $9 \sim 12$, the variations of the calculated trigonal field parameters V , V' and hence of the theoretical spin Hamiltonian parameters change by not more than 4%.

In summary, the spin Hamiltonian parameters and the local structure around the trigonal Co^{2+} center in BGO were theoretically investigated on the basis of an

reasonable off-center displacement of the impurity ion along the C_3 axis.

- [1] B. G. Grabmaier, IEEE Trans. Nucl. Sci. **NS-31**, 372 (1984).
- [2] M. J. Weber, A. C. West, C. Dujardin, B. Rupp, M. Berrondo, and J. F. Rivas-Silva, in *Inorganic Scintillators and Their Applications*, ed. P. Dorenbos et al. University Press, The Netherlands, 1996, p. 234.
- [3] G. Montemezzani, St. Pfandler, and P. Günter, J. Opt. Soc. Amer. **B 9**, 1110 (1992).
- [4] S. K. Kurz and T. T. Perry, J. Appl. Phys. **39**, 3798 (1968).
- [5] A. A. Kaminskii, S. E. Sarkisov, G. A. Denisenko, V. V. Ryabchenkov, V. A. Lomonov, Yu. E. Perlin, M. G. Blazha, D. Schultze, B. Hermoneit, and P. Reiche, Phys. Status Solidi A **85**, 553 (1984).
- [6] E. Moya, L. Contreras, and C. Zaldo, J. Opt. Soc. Amer. **B 5**, 1737 (1988).
- [7] C. Zaldo and E. Diéguez, Opt. Mater. **1**, 171 (1992).
- [8] C. Zaldo, E. Moya, L. F. Magaña, L. Kovačs, and K. Polgaf, J. Appl. Phys. **73**, 2114 (1993).
- [9] A. Martin, D. Bravo, E. Dieguez, and F. J. Lopez, Phys. Rev. B **54**, 12915 (1996).
- [10] D. Bravo, A. Martin, and F. J. Lopez, Solid State Commun. **86**, 281 (1993).
- [11] S. Y. Wu and W. C. Zheng, Phys. Stat. Sol. B **223**, 665 (2001).
- [12] M. L. Du and C. Rudowicz, Phys. Rev. B **46**, 8974 (1992).
- [13] Y. M. Chang, T. H. Yoem, Y. Y. Yeung, and C. Rudowicz, J. Phys.: Condens. Matter **5**, 6221 (1993).
- [14] S. Y. Wu and W. C. Zheng, Phys. Rev. B **65**, 224107 (2002).
- [15] D. J. Newman and B. Ng, Rep. Prog. Phys. **52**, 699 (1989).
- [16] W. L. Yu, X. M. Zhang, L. X. Yang, and B. Q. Zen, Phys. Rev. B **50**, 6756 (1994).
- [17] J. D. Newman, D. C. Pryce, and W. A. Runciman, Am. Mineral. **63**, 1278 (1978).
- [18] D. Bravo and F. J. Lopez, J. Chem. Phys. **99**, 4952 (1993).
- [19] D. J. Segal, R. P. Santoro, and R. E. Newnham, Z. Kristallogr. **123**, 73 (1966).
- [20] A. A. Kaminskii, D. Schultze, B. Hermoneit, S. E. Sarkisov, L. Li, J. Bohm, P. Reiche, R. Ehlert, A. A. Mayer, V. A. Lomonov, and V. A. Balashov, Phys. Status Solidi A **33**, 737 (1976).
- [21] S. Y. Wu, H. N. Dong, and P. Li, Z. Naturforsch. A **58**, 439 (2003).
- [22] H. N. Dong and S. Y. Wu, Z. Naturforsch. A **58**, 507 (2003).
- [23] R. C. Weast, CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton 1989, p. F187.
- [24] E. Clementi and D. L. Raimondi, J. Chem. Phys. **38**, 2686 (1963).
- [25] E. Clementi, D. L. Raimondi, and W. P. Reinhardt, J. Chem. Phys. **47**, 1300 (1967).
- [26] A. A. Mirzakhanyan and A. K. Petrosyan, Sov. Phys. Solid State **28**, 904 (1986).
- [27] J. S. Griffith, The Theory of Transition-Metal Ions, Cambridge University Press, London 1964.
- [28] B. R. McGarvey, J. Chem. Phys. **71**, 51 (1967).
- [29] E. K. Hodgson and I. Fridovich, Biochem. Biophys. Res. Commun. **54**, 270 (1973).
- [30] A. Abragam and M. H. I. Pryce, Prog. Roy. Soc. London A **206**, 173 (1951).
- [31] H. N. Dong, S. Y. Wu, and W. C. Zheng, J. Phys. Chem. Solids **64**, 695 (2003).
- [32] D. Bravot, L. Arizmendit, M. Aguilart, and F. J. Lopez, J. Phys.: Condens. Matter **2**, 10123 (1990).
- [33] R. A. Serway, W. Berlinger, K. A. Muller, and R. W. Collins, Phys. Rev. B **16**, 4761 (1977).