

Electron orbital resonance

K. Katsumata¹ and S. W. Lovesey^{2,3,4}

¹45-11 Kumanochō, Itabashi, Tokyo 173-0025, Japan

²ISIS Facility, STFC, Didcot, Oxfordshire OX11 0QX, United Kingdom

³Diamond Light Source Ltd, Didcot, Oxfordshire OX11 0DE, United Kingdom

⁴Department of Physics, Oxford University, Oxford OX1 3PU, United Kingdom



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A magnetic resonance phenomenon is proposed, in which only the orbital degrees of freedom of electrons participate. This previously unexploited magnetic resonance may be called electron orbital resonance (EOR). To this end, a nonmagnetic, singlet ground state is necessary. In addition, the system needs to exhibit the Van Vleck paramagnetism. Conditions for EOR are met by the rare earth perovskite LaCoO_3 (LCO). The 5D state of LCO is shown to exhibit the van Vleck paramagnetism that result in EOR. The frequency versus magnetic field relation for EOR in LCO is shown to be readily accessible with present day instrumentation. We predict that conventional electron spin resonance signals will be observed in the 5D state of LCO in addition to EOR.

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I. INTRODUCTION

Electron spin resonance (ESR) spectroscopy is firmly established as a valuable tool for investigations of materials at an atomic level of detail. As its name implies, the electron spin is the primary degree of freedom in ESR signals. Orbital degrees of freedom are secondary and enter conventional signals through a spin-orbit interaction [1]. In this paper, we demonstrate that the roles can be reversed, leading to electron orbital resonance (EOR) with orbital degrees of freedom primary. To this end, a nonmagnetic, singlet ground state is necessary. In addition, the system needs to exhibit the Van Vleck paramagnetism [2], the temperature independent paramagnetism originating from excited crystal field levels. We show below that the rare earth perovskite LaCoO_3 (LCO) offers an excellent proving ground for the investigation of EOR.

First, we summarize the magnetic properties of LCO. There has been a number of experimental and theoretical studies on LCO, because of its intriguing and possibly unique magnetic properties [3]. This compound shows a transition from a metallic to semiconducting state in the vicinity of 500 K, together with an anomaly in the magnetic susceptibility χ [4]. With decreasing temperature, χ increases and is at a maximum in the neighborhood of 100 K [4]. Thereafter, χ decreases with decreasing temperature. At low temperatures below ~ 30 K, χ becomes temperature independent, after subtracting the contribution of magnetic impurities [5]. The existence of this temperature independent paramagnetic susceptibility (TIPS) has been confirmed from a nuclear magnetic resonance measurement [5].

We start with an atomic model with localized Co $3d$ orbitals for the magnetic properties of $\text{La}^{3+}\text{Co}^{3+}\text{O}_3^{2-}$ at a low temperature. When a trivalent Co ion ($3d^6$) is placed in an octahedral crystal field, the $3d$ orbital states split into a lower triplet (Γ_5 symmetry type) and upper doublet (Γ_3). In the case of a strong crystal field [1], the six $3d$ electrons are accommodated in the Γ_5 with three up- and three down-spins resulting in a nonmagnetic state named the low-spin (LS)

one [3]. In an intermediate crystal field [1], however, Hund's rules predominate and the ground state of a $3d^6$ system is a 5D . The 5D state of LCO is essentially the same as the high-spin (HS) one discussed in the literature [3]. The ground state of the 5D is nonmagnetic due to a combined effect of crystal field and spin-orbit interaction [6]. It has been shown theoretically that the magnetic properties of LCO are explained with coexisting 5D and LS states [6,7]. As will be shown below, the TIPS in the 5D state is finite, whereas, TIPS does not exist in the LS in its ground state [8].

Okuda *et al.* [9] have observed two types of ESR signals in LCO. The first one (Type I) appears at low temperatures between 4.2 and ~ 35 K, whose intensity decreases with increasing temperature. The origin of the Type I signal has not been explored. The second one (Type II) appears at high temperatures between ~ 25 and ~ 50 K, whose intensity I varies with temperature T as, $I = I_0 \exp(-\Delta E/kT)$, suggesting that the ESR signal comes from the transition within an excited state. Here, I_0 and ΔE are a constant, and k is the Boltzmann constant. A more detailed study of ESR in LCO has been performed by Noguchi *et al.* [10], who presented a phenomenological energy level scheme to explain the Type II signal, in which an excited triplet state lies above a singlet ground state. As reported in Ref. [6], the first excited state in the 5D is a doublet. In order to reconcile the apparent contradiction between the energy level schemes in the 5D state and the one by Noguchi *et al.*, Katsumata proposed that an elementary excitation in the LS state gives an energy level scheme with the first excited quartet above the singlet ground state [6]. It is interesting to study what kind of ESR phenomenon occurs in the 5D state of LCO.

II. EOR IN LaCoO_3

A. The temperature independent paramagnetic susceptibility and the energy level scheme

The energy difference Δ between the Γ_3 and Γ_5 states is typically $\sim 10^4 \text{ cm}^{-1}$ [1], whereas, the energies of the

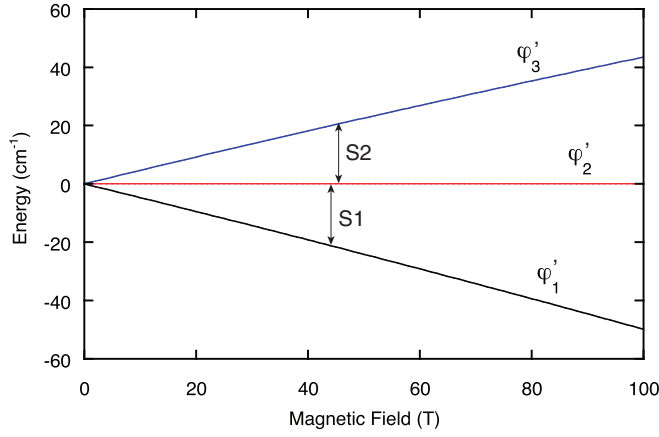


FIG. 1. The magnetic field dependence of the eigenvalues of the Hamiltonian (Eq. (1)) up to second order when $\Delta = 1370 \text{ cm}^{-1}$. Possible magnetic resonance transitions are indicated by arrows. Here, ϕ'_1 , ϕ'_2 , and ϕ'_3 are the eigenfunctions associated with the energy levels.

spin-orbit interaction and the crystal fields of lower symmetry are $\sim 10^2 \text{ cm}^{-1}$ [1]. Therefore, we consider first the contribution of the Γ_3 to Γ_5 , which results in the TIPS and EOR. Then, we discuss the effects of the spin-orbit interaction and crystal field of lower symmetry on the ground state Γ_5 in the next section.

The TIPS comes from the contribution of the excited state to the ground one via the interaction between the orbital angular momentum $\mathbf{L}$ and the applied magnetic field $\mathbf{H}$. In this case the Hamiltonian is given by

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}', \quad (1)$$

where, $\mathcal{H}_0$ represents the crystal field term with cubic symmetry, and

$$\mathcal{H}' = \mu_B \mathbf{L} \cdot \mathbf{H}. \quad (2)$$

In Eq. (2), μ_B is the Bohr magneton. We calculate the eigenvalues of Eq. (1) perturbatively. A detail of the calculation is reported in Ref. [7].

We obtain the eigenvalues W_1 from the first-order perturbation calculation

$$W_1 = 0 \quad (3)$$

and

$$W_1 = \pm \mu_B \sqrt{H_x^2 + H_y^2 + H_z^2} = \pm \mu_B H. \quad (4)$$

When $\mathbf{H} \parallel z$, we obtain the eigenvalues W_2^z from the second-order perturbation calculation

$$W_2^z = 0, \quad (5)$$

and

$$W_2^z = -2\mu_B^2 H_z^2 / \Delta. \quad (6)$$

The TIPS is calculated with the standard method of statistical mechanics using the eigenvalues given above. When $\mathbf{H} \parallel z$ the magnetic susceptibility in zero field χ_0^z is given by [7]

$$\chi_0^z = 8N\mu_B^2 / (3\Delta). \quad (7)$$

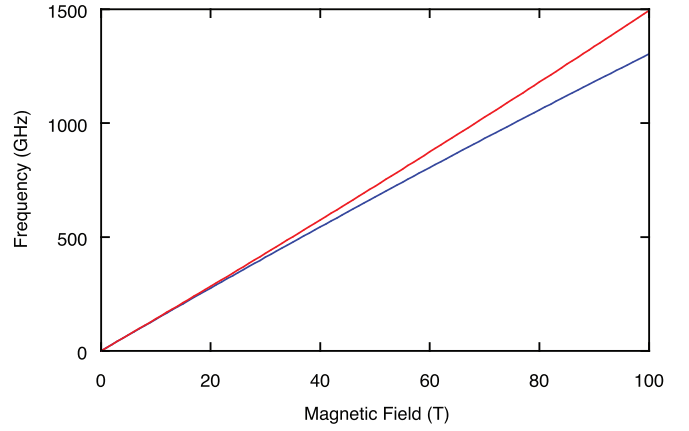


FIG. 2. The frequency dependence of the resonance fields for EOR in LaCoO_3 when $\Delta = 1370 \text{ cm}^{-1}$.

From a comparison of Eq. (7) with the measured value [5], we obtain, $\Delta = 1.37 \times 10^3 \text{ cm}^{-1}$.

We have from Eqs. (3), (4), (5), and (6), the magnetic field dependence of the eigenvalues up to second order as shown in Fig. 1.

B. The frequency versus magnetic field diagram

Figure 2 shows the frequency dependence of the resonance fields derived from Fig. 1. We see two resonance branches, the frequencies of which are given by $\mu_B H (1 \pm 2\mu_B H / \Delta)$. A salient feature of this new resonance is that its g factor is $g = 1$, in contrast to the case of electron paramagnetic resonance (EPR), which usually gives $g \simeq 2$. The reason for observing $g = 1$ is that only orbital degrees of freedom participate in the present case.

C. The intensity of the EOR signal

We estimate the intensities of the resonance lines S1 and S2 in Fig. 1. The transition probabilities per unit time $w(\text{S1})$ and $w(\text{S2})$ for the S1 and S2 signals are given, respectively, by [11]

$$w(\text{S1}) = (4\pi^2/h)\rho(\phi'_2)|\langle\phi'_2|\mu_B h_{\text{res}} L'_x|\phi'_1\rangle|^2, \quad (8)$$

and

$$w(\text{S2}) = (4\pi^2/h)\rho(\phi'_3)|\langle\phi'_3|\mu_B h_{\text{res}} L'_x|\phi'_2\rangle|^2, \quad (9)$$

where, h is Planck's constant, $\rho(\phi)$ the energy density in the ϕ state and h_{res} is the amplitude of electromagnetic wave applied perpendicularly to $\mathbf{H}$. The quantity L'_x appearing in Eqs. (8) and (9) is calculated as follows: The basis functions ϕ_1, ϕ_2 and ϕ_3 belonging to the Γ_5 , and ϕ_4 and ϕ_5 belonging to the Γ_3 are related to the basis functions $|2\rangle, |1\rangle, |0\rangle, |-1\rangle$ and $|-2\rangle$ belonging to the 5D state by the following transformation R [6]:

$$R = \begin{pmatrix} 0 & -\sqrt{1/3} & 0 & 0 & \sqrt{2/3} \\ 0 & 0 & 1 & 0 & 0 \\ -\sqrt{2/3} & 0 & 0 & -\sqrt{1/3} & 0 \\ 0 & \sqrt{2/3} & 0 & 0 & \sqrt{1/3} \\ \sqrt{1/3} & 0 & 0 & -\sqrt{2/3} & 0 \end{pmatrix}. \quad (10)$$

The x component L_x of the orbital angular momentum $\mathbf{L}$ transforms as

$$L'_x = RL_x R^{-1} = \begin{pmatrix} 0 & -1/\sqrt{2} & 0 & 0 & -1 \\ -1/\sqrt{2} & 0 & -1/\sqrt{2} & 1 & -1 \\ 0 & -1/\sqrt{2} & 0 & -1 & 0 \\ 0 & 1 & -1 & 0 & 0 \\ -1 & -1 & 0 & 0 & 0 \end{pmatrix}. \quad (11)$$

The eigenfunctions φ'_1 , φ'_2 and φ'_3 in Eqs. (8) and (9) are slightly different from the unperturbed ones, because of an admixture from the Γ_3 state due to the perturbing Hamiltonian [Eq. (2)]. Since the amount of the admixture is $\sim \mu_B H / \Delta$, which is ~ 0.03 at $H = 100$ T and $\Delta = 1370$ cm $^{-1}$, we may disregard the admixture in calculating the transition probability. From Eqs. (8), (9), and (11), we obtain

$$w(S1) \simeq (2\pi^2/h)\rho(\varphi'_2)(\mu_B h_{\text{res}})^2, \quad (12)$$

and

$$w(S2) \simeq (2\pi^2/h)\rho(\varphi'_3)(\mu_B h_{\text{res}})^2, \quad (13)$$

Since we expect that $\rho(\varphi'_2)$ and $\rho(\varphi'_3)$ are nearly the same magnitude, the transition probabilities for the S1 and S2 signals are finite with nearly the same value.

The temperature dependence of the intensities of the S1 and S2 signals is calculated with the standard procedure [1]. The intensities decrease monotonically with increasing temperature.

III. ESR IN THE 5D STATE OF LaCoO_3

A. The energy level scheme

The energy level scheme in the 5D state of LCO has been discussed before [6]. When $\mathbf{H}$ is applied parallel to the z axis, the Hamiltonian is given by

$$\mathcal{H} = -\lambda' \mathbf{l} \cdot \mathbf{S} + 9B_2^0(l_z^2 - 2/3) - 80B_4^0(l_z^2 - 9/10) + \mu_B H(2S_z - l_z), \quad (14)$$

where, λ' is the spin-orbit interaction constant, $\mathbf{l}$ the fictitious orbital angular momentum of magnitude one, $\mathbf{S}$ the spin angular momentum of magnitude two, B_2^0 and B_4^0 the magnitudes of the crystal field due to the trigonal distortion. Since $l_z + S_z$ commutes with the Hamiltonian, its eigenvalue m can be used to classify the states. We denote the states by $|l_z, S_z\rangle$, where l_z and S_z take three and five states, respectively. Then, we have 15 energy levels in total; one $m = 3$, two $m = 2$, three $m = 1$, three $m = 0$, three $m = -1$, two $m = -2$ and one $m = -3$ states.

Figure 3 shows the lowest and second lowest eigenvalues of the Hamiltonian [Eq. (14)] as a function of the applied magnetic field when $\lambda' = -410$ cm $^{-1}$, $\delta(\equiv 3B_2^0) = 1800$ cm $^{-1}$ and $\varepsilon(\equiv 8B_4^0) = 300$ cm $^{-1}$. We see that the ground state is a singlet with an energy gap to the first excited doublet at low

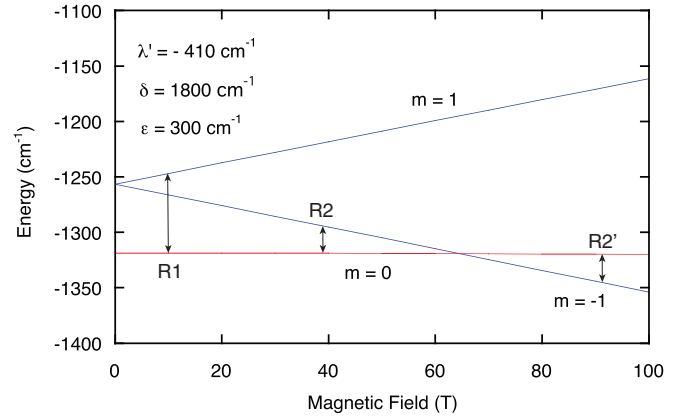


FIG. 3. The magnetic field dependence of the lowest and second lowest energy levels of the 5D state of LaCoO_3 when $\lambda' = -410$ cm $^{-1}$, $\delta(\equiv 3B_2^0) = 1800$ cm $^{-1}$ and $\varepsilon(\equiv 8B_4^0) = 300$ cm $^{-1}$. Possible ESR transitions designated R1, R2, and R2' are indicated by arrows.

fields. ESR transitions are allowed between the two states with difference in the magnetic quantum number $\Delta m = \pm 1$.

B. The frequency versus magnetic field diagram

In Fig. 4, is shown the frequency dependence of the resonance fields derived from Fig. 3. We see three resonance branches designated R1, R2, and R2'. The two modes R1 and R2 are degenerated in zero field at the frequency 1.86 THz, reflecting the energy gap mentioned above. The resonance frequency of the R2 mode becomes zero at $H = 64.6$ T.

C. The intensity of the ESR signal

We calculate the intensities of the ESR signals of the R1 and R2 modes. Similarly to the discussion in Sec. II, the transition probability per unit time w from the initial $|i\rangle$ to the final $|f\rangle$ states is given by

$$w = (4\pi^2/h)\rho(f)|\langle f|\mathcal{H}''|i\rangle|^2, \quad (15)$$

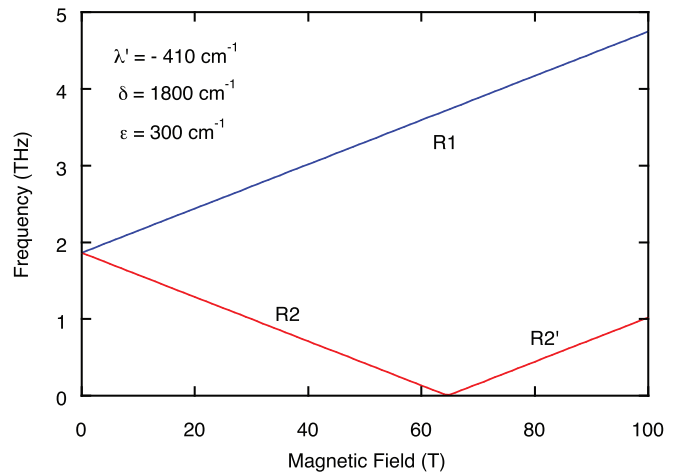


FIG. 4. The frequency dependence of the resonance fields of the ESR signals in the 5D state of LaCoO_3 when $\lambda' = -410$ cm $^{-1}$, $\delta(\equiv 3B_2^0) = 1800$ cm $^{-1}$ and $\varepsilon(\equiv 8B_4^0) = 300$ cm $^{-1}$.

where, $\mathcal{H}''$ is given, in the present case, as

$$\mathcal{H}'' = \mu_B h_{\text{res}}(-l_x + 2S_x). \quad (16)$$

From Eqs. (15) and (16), the probabilities $w(\text{R1})$ and $w(\text{R2})$ of the ESR signals designated R1 and R2 in Fig. 4 are given, respectively, by

$$w(\text{R1}) = (4\pi^2/h)(\mu_B h_{\text{res}})^2 \rho(m=1) \times |\langle m=1 | -l_x + 2S_x | m=0 \rangle|^2, \quad (17)$$

and

$$w(\text{R2}) = (4\pi^2/h)(\mu_B h_{\text{res}})^2 \rho(m=-1) \times |\langle m=-1 | -l_x + 2S_x | m=0 \rangle|^2. \quad (18)$$

We calculate the expectation values in Eqs. (17) and (18). The $m=0$ state is a linear combination of $|l_z=1, S_z=-1\rangle$, $|l_z=0, S_z=0\rangle$ and $|l_z=-1, S_z=1\rangle$ given by

$$|m=0\rangle = a|1, -1\rangle + b|0, 0\rangle + c|-1, 1\rangle, \quad (19)$$

where, a , b , and c are constants. From the condition that a , b , and c are nonzero, we have a 3×3 secular determinant. Using *Mathematica*'s command, Eigensystem[], we obtain the eigenvalue and the associated coefficients a , b , c simultaneously. When $H = 10$ T, we obtain $E(m=0) = -1318 \text{ cm}^{-1}$ and $\{a, b, c\} = \{0.2737, -0.9229, 0.2705\}$.

The $m=1$ state is given by

$$|m=1\rangle = j|1, 0\rangle + n|0, 1\rangle + p|-1, 2\rangle, \quad (20)$$

where, j , n and p are constants. We obtain $E(m=1) = -1247 \text{ cm}^{-1}$ and $\{j, n, p\} = \{0.2409, -0.9303, 0.2766\}$ at $H = 10$ T.

The $m=-1$ state is given by

$$|m=-1\rangle = q|1, -2\rangle + u|0, -1\rangle + v|-1, 0\rangle, \quad (21)$$

where, q , u , and v are constants. For $H = 10$ T, we obtain $E(m=-1) = -1266 \text{ cm}^{-1}$ and $\{q, u, v\} = \{-0.2804, 0.9298, -0.2383\}$.

From Eqs. (19) and (20)

$$\begin{aligned} |\langle m=1 | -l_x + 2S_x | m=0 \rangle|^2 \\ = (2cp^* - cn^*/\sqrt{2} + \sqrt{6}aj^* - bj^*/\sqrt{2} + \sqrt{6}bn^*)^2, \end{aligned} \quad (22)$$

where, the asterisk indicates the complex conjugate. We note that the coefficients take real numbers in the present case. Inserting the numerical values obtained above to Eq. (22), we have at $H = 10$ T

$$|\langle m=1 | -l_x + 2S_x | m=0 \rangle|^2 = 7.56. \quad (23)$$

From Eqs. (19) and (21)

$$\begin{aligned} |\langle m=-1 | -l_x + 2S_x | m=0 \rangle|^2 \\ = (2aq^* - au^*/\sqrt{2} + \sqrt{6}bu^* - bv^*/\sqrt{2} + \sqrt{6}cv^*)^2. \end{aligned} \quad (24)$$

Replacing $a, b, c, \dots$ in Eq. (24) by the numerical values obtained above, we have at $H = 10$ T

$$|\langle m=-1 | -l_x + 2S_x | m=0 \rangle|^2 = 7.56. \quad (25)$$

As is seen from Eqs. (17), (18), (23), and (25), the intensities of the ESR signals are finite with the same magnitude.

The temperature dependence of the intensities of the R1 and R2 signals is calculated with the standard procedure [1]. The intensities decrease monotonically with increasing temperature.

IV. DISCUSSION AND CONCLUSIONS

As explained above, the ground state of the 5D in LCO is a singlet with an energy gap to the first excited state. As a result, the magnetism disappears at low temperatures. In this nonmagnetic state, a fraction of orbital angular momentum persists which comes from the excited orbital state Γ_3 assisted by the interaction given by Eq. (2) and gives the TIPS and EOR. In order to observe EOR, the measurement should be performed at low temperatures well below the temperature at which χ shows a peak. In the case of LCO, the measurement should be done at $T \ll 100$ K.

The magnetic field dependence of the resonance frequency for the EOR is given by $\mu_B H(1 \pm 2\mu_B H/\Delta)$. At low frequencies and low magnetic fields, one may easily observe the signal with $g = 1$. It is interesting to test whether or not a deviation in the g factor from $g = 1$ exists, in relation to the case of electron spin [12]. EOR is not restricted to LCO. The magnetic materials with a singlet ground state that is nonmagnetic such as CsFeCl_3 [13] and some rare-earth compounds [14] are candidates for observing EOR, provided that TIPS exists in these materials.

The Hamiltonian for the 5D state [Eq. (14)] contains three parameters, λ' , $\delta(\equiv 3B_2^0)$ and $\varepsilon(\equiv 8B_4^0)$. The values given in the caption to Fig. 3 are determined from the analysis of the magnetization data [6]. ESR measurements will give a more accurate value for these parameters. The frequency and magnetic field ranges of ESR spectrometer have been expanding and now a spectrometer operating up to 1.1 THz is available [15]. When this spectrometer is used in combination with a magnet operating at ~ 35 T, the R2 mode in Fig. 4 will be observed. Alternatively, one may use a far-infrared spectrometer to observe magnetic excitations at high frequencies [16].

In summary, a previously unexploited magnetic resonance phenomenon is proposed, in which only the orbital degrees of freedom of electrons participate. This new magnetic resonance is named electron orbital resonance (EOR). To observe EOR, a nonmagnetic, singlet ground state is necessary. In addition, the system needs to exhibit the Van Vleck paramagnetism. Conditions for EOR are met by the rare earth perovskite LaCoO_3 (LCO). EOR may elucidate the orbital state of novel materials, such as, quantum antiferromagnets and strongly correlated electron systems. We have also discussed conventional electron spin resonance signals expected for the 5D state of LCO.

- [1] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Oxford University Press, Oxford, 1970).
- [2] J. H. van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).
- [3] Y. Kobayashi, K. Sato, and K. Asai, in *Spin-Crossover Phenomena in Perovskite Cobaltites: Their History and Current Status of the Research*, edited by Y. Okimoto, T. Saitoh, Y. Kobayashi, and S. Ishihara, Springer Series in Materials Science Vol. 305 (Springer, Singapore, 2021).
- [4] R. R. Heikes, R. C. Miller, and R. Mazelsky, *Physica* **30**, 1600 (1964).
- [5] M. Itoh, M. Sugahara, I. Natori, and K. Motoya, *J. Phys. Soc. Jpn.* **64**, 3967 (1995).
- [6] K. Katsumata, *Phys. Rev. B* **106**, L020406 (2022).
- [7] K. Katsumata and S. W. Lovesey, *J. Phys.: Condens. Matter* **36**, 125803 (2024).
- [8] J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.* **53**, 601 (1957).
- [9] K. Okuda, S. Kawamata, K. Nakahigashi, H. Ishibashi, M. Hayashi, H. Ohta, H. Nojiri, and M. Motokawa, *J. Magn. Magn. Mater.* **177-181**, 1375 (1998).
- [10] S. Noguchi, S. Kawamata, K. Okuda, H. Nojiri, and M. Motokawa, *Phys. Rev. B* **66**, 094404 (2002).
- [11] L. I. Schiff, *Quantum Mechanics*, 3rd ed. (McGraw-Hill, New York, 1970).
- [12] J. Schwinger, *Phys. Rev.* **73**, 416 (1948).
- [13] H. Yoshizawa, W. Kozukue, and K. Hirakawa, *J. Phys. Soc. Jpn.* **49**, 144 (1980).
- [14] G. T. Trammell, *Phys. Rev.* **131**, 932 (1963).
- [15] G. Khatri, G. Fritjofson, J. Hanson-Flores, J. Kwon, and E. D. Barco, *Rev. Sci. Instrum.* **94**, 034714 (2023).
- [16] H. Yamaguchi, K. Katsumata, M. Hagiwara, M. Tokunaga, H. L. Liu, A. Zibold, D. B. Tanner, and Y. J. Wang, *Phys. Rev. B* **59**, 6021 (1999).