Crystal-Field Paschen-Back Effect on Ruby in Ultrahigh Magnetic Fields

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Zeeman spectra of the R lines of ruby (Cr3+: α-Al2O3) were studied in ultrahigh magnetic fields up to 230 T by magneto-photoluminescence measurements. The observed Zeeman patterns exhibit nonlinear behaviors at above 100 T, evidencing the breakdown of the previously reported Paschen-Back effect for \( B \perp c \) geometry. We adopted the crystal-field multiplet theory including the cubic crystal field \( \mathcal{H}_{\text{cube}} \), the trigonal crystal field \( \mathcal{H}_{\text{trig}} \), the spin-orbit interaction \( \mathcal{H}_{\text{SO}} \), and the Zeeman interaction \( \mathcal{H}_Z \). It is found that the nonlinear splitting of the R lines is owing to the hybridization between the \( ^2E \) and \( ^2T_1 \) states, which leads to the quantization of these Zeeman levels with the orbital angular momentum. Our results suggest that the exquisite energy balance among \( \mathcal{H}_{\text{cube}}, \mathcal{H}_{\text{trig}}, \mathcal{H}_{\text{SO}}, \) and \( \mathcal{H}_Z \) realized in ruby offers a unique opportunity to observe the onset of the crystal-field Paschen-Back effect toward the high-field extreme.

Zeeman effect is categorized into anomalous Zeeman (AZ) effect at the weak-field limit and normal Zeeman (NZ) effect at the high-field limit. When atoms are located in weak magnetic fields, the energy levels split nonlinearly due to the competition between the external magnetic field and the hyperfine or the spin-orbit interactions. Under high magnetic fields where the Zeeman energy far exceeds those interactions, on the other hand, the energy splitting is asymptotically quantized by \( \mu_B B \), where \( \mu_B \) is the Bohr magneton and \( B \) is the magnetic field.

Historically, the crossover from the AZ effect to the NZ effect, the so-called Paschen-Back (PB) effect [1], has been observed in various atoms [2–8] and molecules [9, 10]. For example, the D lines of the sodium atom exhibit the hyperfine PB effect around 30 mT [4, 5] and the spin-orbit PB effect around 50 T [6]. Through this process, the good quantum number changes from \( M_F \) for the total angular momentum of an atom to \( M_I \) and \( M_J \) for that of a nucleus and electrons, respectively, and then \( M_I \) and \( M_J \) are further decoupled to \( M_L \) and \( M_S \) for the orbital and spin angular momenta, respectively.

The PB effect can also be observed in solid states [11–16]. The most well-known example is the R lines of ruby [13–16]. Many spectroscopic works on ruby have been done for more than half century, motivated by the scientific interests [13–27] as well as its applications to a solid-state laser and pressure gauge [28–33]. The optical transitions of ruby stem from the \( \text{Cr}^{3+} \) impurities in \( \alpha\text{-Al}_2\text{O}_3 \), where \( \text{Cr}^{3+} \) ions are subjected to the strong cubic crystal field of the octahedrally coordinated \( \text{O}^{2−} \) ions. Furthermore, the repulsion between neighboring cations causes the slight lattice distortion, lowering the symmetry to trigonal \( C_3 \) (In the following, we take the trigonal axis as \( c \) axis). As shown in Fig. 1(a), the absorption spectrum of ruby in visible region consists of two broad bands and three groups of sharp lines. In the notation of the cubic symmetry, the R lines correspond to an electric dipole transition from the ground state \( ^4A_2 \) to the first excited state \( ^2E \), appearing at around 1.79 eV (694 nm). Due to the interplay of the trigonal crystal field and the spin-orbit interaction, the \( ^2E \) state further splits into two Kramers doublets \( ^2E \) and \( 2\mathcal{A} \) (R1 and R2 lines) with the energy gap of \( \delta = 3.6 \) meV. The observed Zeeman patterns of the R lines up to 60 T agree well with the theory shown in Figs. 1(b) and 1(c) [15–18]. Here, eight optically allowed transitions for \( E \perp c \) are noted for each \( B \parallel c \) and \( B \perp c \) geometry. For \( B \parallel c \), the tendency of the PB effect is observed toward 60 T, where the Zeeman energy is large enough compared to the initial splitting (\( g\mu_B B = 2\delta \)), where \( g = 2 \) [15, 16].

This PB effect in ruby can be understood as such, that the \( \text{Cr}^{3+} \) spins initially oriented along the \( c \) axis are gradually quantized along the applied magnetic field \( B \perp c \). Unlike (Fig. 1. (a) Absorption spectrum of ruby in visible region and the local structure of \( \text{CrO}_6^{3−} \) with the \( C_3 \) symmetry. The corresponding excited state from the ground state \( ^4A_2 \) is denoted for each absorption peak. (b)(c) Energy diagrams of the Zeeman splitting of the R lines for (b) \( B \parallel c \) and (c) \( B \perp c \) geometries. A small initial splitting of 0.05 meV in the \( ^4A_2 \) state is neglected. Optically allowed transitions for \( E \perp c \) are denoted by A, B, ..., P. In the PB region for \( B \perp c \), the excited levels asymptotically approach the dashed straight lines.)
The measurements were performed at around 200 K by using the case of isolated atoms, the Zeeman levels of the R lines (FWHM) of the fitted Lorentzian function due to the ambiguity of the peak assignments. Inset in (b) presents the average of the peak shifts with the magnetic field, reflecting the experimental peak positions [Additional data not shown in (a) are also plotted]. Red and blue lines show the theoretical curves obtained from the crystal-field multiplet theory (see text for details). Inset in (b) presents the average of the peak shifts with the magnetic field, reflecting the change in the mean energy of the four Zeeman levels splitting from the $^2E$ state. Error bars in (c) are set from the full width at half maximum (FWHM) of the fitted Lorentzian function due to the ambiguity of the peak assignments.

In this Letter, we present the Zeeman spectra of the R lines of ruby in ultrahigh magnetic fields up to 230 T. For both $\mathbf{B} \parallel c$ and $\mathbf{B} \perp c$ geometries, the observed Zeeman patterns exhibit nonlinear splitting at above 100 T, already beyond the previous theory based on the effective Hamiltonian for the $^2E$ state [17, 18]. The observed Zeeman patterns are analyzed by the standard crystal-field multiplet theory including the cubic crystal field, the trigonal crystal field, the spin-orbit interaction, and the Zeeman interaction [17–19, 34–37]. The hybridizations between the $^2E$ and the upper excited states, which are responsible for the AZ effect at above 100 T, are discussed. We also refer to the Zeeman spectra at the high-field extreme and the possible crystal-field PB effect.

The magneto-photoluminescence (PL) measurements were carried out by using a horizontal single-turn-coil (HSTC) megagauss generator. Disk-shaped ruby samples with 2.5 mm diameter and 1.0 mm thickness (SHINKOSHA Co., Ltd.) were used. The concentration of the Cr$^{3+}$ ion was 0.70 wt%, which is low enough to neglect the effect of the exchange interaction. The magnetic fields were measured by a calibrated pickup-coil with the error of $\pm 2\%$. The 532 nm laser was used for the excitation $^4A_2 \rightarrow ^4T_2$, and the PL spectra were measured by the high-speed streak camera. In our setup, the incident light is polarized as $\mathbf{E} \perp c$ for $\mathbf{B} \parallel c$, while both $\mathbf{E} \perp c$ and $\mathbf{E} \parallel c$ components are mixed for $\mathbf{B} \perp c$. The measurements were performed at around 200 K by using $^4$He-flow-type cryostats. In this temperature range, electrons are thermally distributed within the $^2E$ levels and almost all of the optically allowed transitions are observed as relatively sharp peaks. Exceptionally, the measurements at above 190 T were performed without using the cryostat due to the limited space inside the STC. For the best signal-to-noise ratio, we performed several cycles of measurements with the different maximum field $B_{\text{max}}$ and integrated the spectra recorded near $B_{\text{max}}$ within 1 % for each pulse. Details of the setup and analysis are found in Supplemental Material [38].

Our main results are summarized in Fig. 2. The evolution of the R lines’ Zeeman spectra are shown in Fig. 2(a). The peak positions as a function of magnetic field for $\mathbf{B} \parallel c$ and $\mathbf{B} \perp c$ are plotted in Figs. 2(b) and 2(c), respectively, which are extracted by multi-Lorentzian fits. The energy shift $\Delta E$ is measured from the center of the R1 and R2 lines at zero field. For $\mathbf{B} \parallel c$, all of the eight optically allowed lines, corresponding to A–H in Fig. 1(b), are clearly observed. Remarkably, the Zeeman patterns deviate from the linear field-dependence to the lower energy side as the magnetic field increases, resulting in the shift of the average peak position as shown in the inset of Fig. 2(b). For $\mathbf{B} \perp c$, three distinct peaks are observed at 91 T, which can be understood that six lines, corresponding to J–O in Fig. 1(c), merge into three lines in the previously reported PB region. Note that the rest two lines, I and P, are hardly observable due to the little transition probability under high magnetic fields [14]. Surprisingly, those three peaks split again into (at least) six peaks at above 100 T, contradicting the concept of the previously reported PB effect. The tendency of the peak shifts to the lower energy side is also seen as in the case of $\mathbf{B} \parallel c$. 

![Figure 2](image-url)
To the best of our knowledge, there is no prediction that the AZ effect emerge at around 100 T for the R lines of ruby. For explaining the Zeeman patterns of the R lines, a simple effective Hamiltonian for the $^2E$ state has been so far considered [14–18]. For $\mathbf{B} \parallel c$, the Zeeman patterns of the $R_1$ and $R_2$ lines in the low-field region can be respectively discribed by $E_{1\pm}(B) = -\frac{g}{2} \pm \frac{1}{2}(g_0 + 2g_{||})\mu_B B$ and $E_{2\pm}(B) = -\frac{g}{2} \pm \frac{1}{2}(g_0 - 2g_{||})\mu_B B$ [see Fig. 1(b)]. Here, $g_0 = 1.98$ \cite{21} is the $g$-factor of the ground state, and $g_{||} = 0.23$ and $g_{\perp} = 0.26$ \cite{16} are the $g$-shifts which are mainly caused by the third-order interactions between the $^2E$ and the upper excited states, $^2T_1$ and $^2T_2$, through the trigonal crystal field and the orbital angular momentum along the c axis ($L_c$) \cite{18}.

For $\mathbf{B} \perp c$, in contrast, the Zeeman patterns are described by the quadratic relations without lifting the degeneracies of the Kramers doublets as $E_{1\pm}(B) = -(1/2)\sqrt{\delta^2 + (g_0 \mu_B B)^2}$ and $E_{2\pm}(B) = (1/2)\sqrt{\delta^2 + (g_0 \mu_B B)^2}$ [see Fig. 1(c)]. As is evident from these formula, this model assumes that the center of the four energy levels remains constant even in the external magnetic field. This contradicts our experimental observations at above 100 T, indicating that the hybridization between the $^2E$ and the upper excited states need to be directly incorporated rather than perturbatively treated.

Accordingly, we adopted a general multiplet Hamiltonian comprised of all the 120 bases in the $3d^3$ state. In this Hamiltonian, the trigonal crystal field ($H_{\text{trig}}$), the spin-orbit interaction ($H_{\text{SO}}$), and the Zeeman interaction ($H_Z$) were involved in together with the cubic crystal field ($H_{\text{cubic}}$). The bases are expressed as $| (\alpha \Sigma \Gamma) M_\Sigma \rangle$, where $\alpha$ is the electronic configuration, $M_\Sigma$ the spin quantum number in the spin-$\Sigma$ state, and $\Gamma$ the orbital function in the cubic irreducible representation $\Gamma$. We take $M_\Sigma$ and $\Gamma$ quantized along the trigonal $c$ axis ($u_z$ for $E$, $a_y$ and $a_0$ for $T_1$, and $x_{\pm}$ and $x_0$ for $T_2$) \cite{17, 18}. In the following, the notation $\Sigma \Gamma$ is omitted if it is evident from the context.

Several empirical parameters were introduced in the multiplet Hamiltonian for numerical diagonalization: the cubic crystal-field strength $10D_q$. Racah parameters $B$ and $C$ \cite{34}, the trigonal crystal fields $K$ and $K'$ defined as $K \equiv \langle (t_2) + \frac{1}{2}x_1^2 \rangle H_{\text{trig}} [(t_2) + \frac{1}{2}x_1^2]$ and $K' \equiv -(1/\sqrt{2}) \langle (t_2) + \frac{1}{2}x_1^2 \rangle H_{\text{trig}} [(t_2) + \frac{1}{2}u_\perp]$, the spin-orbit interactions $\zeta$ and $\zeta'$ defined as $\zeta \equiv -2 \langle (t_2) + \frac{1}{2}x_1^2 \rangle H_{\text{SO}} [(t_2) + \frac{1}{2}x_1^2]$ and $\zeta' \equiv -\sqrt{2} \langle (t_2) + \frac{1}{2}x_1^2 \rangle H_{\text{SO}} [(e) + \frac{1}{2}u_\perp]$, and the orbital reduction factors $k$ and $k'$ defined as $k \equiv -\langle (t_2) + \frac{1}{2}x_1^2 \rangle L_z [(t_2) + \frac{1}{2}x_1^2]$ and $k' \equiv -(1/\sqrt{2}) \langle (t_2) + \frac{1}{2}x_1^2 \rangle L_z [(e) + \frac{1}{2}u_\perp]$, which reflect the Cr-O bond covalency. Note that $K$, $K'$, $\zeta$, $\zeta'$, $k$, and $k'$ are the matrix elements between one-electron states, and $K = K'$, $\zeta = \zeta'$, and $k = k'$ is expected to be true for the free ion. Similar theoretical approach focusing on the low-field limit was attempted previously, but the discrepancies between experimental and theoretical values of $\delta$ and $g$-factor are relatively large \cite{19, 20}. Hence, although no perfect quantitative match seems to be achieved with any set of parameters, reexamination of the appropriate values was required in this work. We chose the parameters in $H_{\text{cubic}}$ as $10D_q = 2.320 \text{ eV}$, $B = 0.071 \text{ eV}$, and $C = 0.422 \text{ eV}$ following the latest analysis in Ref. \cite{27}, which succeeded in reproducing the spectrum of ruby at zero field in a wide energy range including the UV region. Then, we searched for the combination of the values of $K$, $K'$, $\zeta$, $\zeta'$, $k$, and $k'$ which simultaneously satisfy (i) the initial splitting $\delta = 3.6 \text{ meV}$, (ii) the $g$-values of the $R_1$ and $R_2$ lines for $\mathbf{B} \parallel c$ in the low-field limit, $g_0 + 2g_{||} = 2.44$ and $g_0 - 2g_{||} = 1.46$ \cite{16}, and (iii) our new experimental results in the high-field region. Here, we imposed additional constraints of $K < 0$, $\zeta > 0$, $0 < K' < 1$, $0.8 < \zeta'/\zeta < 1$, and $k'/k = \zeta'/\zeta$.

The calculated energy diagrams of the four Zeeman levels are shown up to 250 T in Figs. 3(a) and 3(b). The parameters are chosen as $K = -0.037 \text{ eV}$, $K' = -0.013 \text{ eV}$, $\zeta = 0.025 \text{ eV}$, $k = 0.72$, and $k'/k = \zeta'/\zeta = 0.86$. Here, $K$ and $K'$ are a bit smaller compared to those in the previous works, whereas $\zeta$ and $\zeta'$ are consistent \cite{19, 20, 27}. It can be seen that all of the four curves for each geometry show upwardly convex magnetic field dependence at above 100 T. These trends can be clearly captured as the decrease in the field-derivatives of the energy $g_2 \equiv \frac{dE}{dB}(r = 1, \pm 2)$ as shown in Figs. 3(c) and 3(d). Furthermore, for $\mathbf{B} \perp c$, the splitting of each Kramers doublet starts to be clearly seen at around 100 T and becomes larger toward higher fields as shown in Fig. 3(b). The ground state $^3A_2$ is found to show the nearly linear Zeeman splitting up to 250 T (not shown). From the above, the theoretical Zeeman patterns of the R lines are obtained as shown in Figs. 2(b) and 2(c), which agree well with the experimental peak plots for both geometries. This indicates that the semipiempirical crystal-field multiplet Hamiltonian taking all the bases in the $3d^3$ state can account for the Zeeman spectra of the R lines of ruby even in the megagauss region.

As shown in Fig. 2(c), our calculation predicts that each of the three merged peaks at around 100 T splits into four indvidual peaks beyond the previously reported PB region for $\mathbf{B} \perp c$. All of them are optically allowed, suggesting that the observed PL spectra at about 100 T are composed of 12 peaks, while not all lines are well resolved due to their overlapping.

![FIG. 3. (a)(b) Calculated energy diagrams of the four Zeeman levels splitting from the $^2E$ states with the magnetic field up to 250 T for (a) $\mathbf{B} \parallel c$ and (b) $\mathbf{B} \perp c$ geometries. (c)(d) The corresponding field-derivatives of the energy for (c) $\mathbf{B} \parallel c$ and (d) $\mathbf{B} \perp c$ geometries.](image-url)
In this work, those spectra are tentatively fitted by six peaks with relatively large errors because the peak assignments with the 12-peak fit are challenging within our experimental accuracy. In Supplemental Material, we give a detailed analysis of the experimental and theoretical peak intensities [38].

Next, we discuss the wave functions of these four levels in magnetic fields. The wave functions are expressed by a linear combination of the 120 bases in the 3d$^3$ state, $|\varphi_\ell \rangle = \sum_c c_\ell |(\alpha \tau S T)M_S \gamma \rangle$, where $c_\ell$ is a complex number coefficient. Our calculation reveals that $|\varphi_{1\pm} \rangle (|\varphi_{2\pm} \rangle)$ at zero field mainly consists of one base $| (t_2^2 E) \pm 1/2 u_z \rangle ((t_2^2 E) \pm 1/2 u_z \rangle)$ with $|c_\ell|^2 = 0.947 (0.941)$ [39]. When a magnetic field is applied, the second excited states $^2T_1$ start to hybridize with the $^2E$ states in the first order via the orbital term of $\mathcal{H}_Z$. Note that the $^2T_1$ states are composed of three Kramers doublets, all of which are $\Delta = 60 \sim 90$ meV away from the $^2E$ states [40]. The field dependences of $|c_\ell|^2$ for the $^2E$ and $^2T_1$ states up to 250 T are summarized in Fig. 4, where only the crucial components are shown. For $\mathbf{B} \parallel c$, as shown in Figs. 4(a)–4(d), the main component of the $^2E$ states decreases in each of the four wave functions, associated with the increase in the contribution of the $^2T_1$ states with the same $M_L$ and $M_S$. Meanwhile, their field-dependences in $|\varphi_{2\pm} \rangle$ and $|\varphi_{1\pm} \rangle$ are different from those in $|\varphi_{1\pm} \rangle$ and $|\varphi_{2\pm} \rangle$. This is responsible for the difference in the field dependence of $g'$, exhibiting convex upward and downward behaviors, respectively [see Fig. 3(c)]. In contrast, for $\mathbf{B} \perp c$, both the summation of the $|+1/2u_z\rangle$ and $|-1/2u_z\rangle$ components and that of the $|+1/2u_z\rangle$ and $|-1/2u_z\rangle$ components approach 0.5 toward high magnetic fields as shown in Figs. 4(e)–4(h). These features signal the tendency of the quantization of the spin along the field direction, i.e. the previously reported PB effect [14]. Besides, as shown in Figs. 4(i)–4(l), we see that the $|\pm 1/2\rangle$ components significantly increase only in $|\varphi_{2\pm} \rangle$ and $|\varphi_{1\pm} \rangle$. They are related to the lowest energy level of the three Kramers doublets of the $^2T_1$ states. Therefore, the hybridization of those components is responsible for the shift of $E_{1\pm}$ and $E_{1\pm}$ to lower energy than $E_{2\pm}$ and $E_{2\pm}$, respectively [see Fig. 3(b)].

These detailed theoretical analyses enable us to get more insights about the Zeeman patterns in ultrahigh magnetic fields. As previously reported, the Zeeman patterns of the R lines exhibit (almost) linear behaviors around 60 T. This is because of the special energy relations among the initial level splittings and the Zeeman energy, $\delta \ll H_Z \ll \Delta$, where the hybridization between the first and second excited states $^2E$ and $^2T_1$ is negligible. However, their interactions are already important at above 100 T, resulting in the nonlinear behaviors that are experimentally observable. Indeed, our calculation suggests that $2 \sim 12\%$ of the $^2T_1$ components are contributing to the R lines at 250 T as is seen from Figs. 4(a)–4(d) and Figs. 4(i)–4(l). In the field region of $10^3$ T, where $\Delta < H_Z \ll 10^4 q$ is achieved, the $^2E$ and $^2T_1$ states are completely mixed. Importantly, both of them do not directly interact with the higher excited states $^4T_2$, $^2T_2$, and $^4T_1$ shown in Fig. 1(a) via the orbital term of $\mathcal{H}_Z$. Thus, the Zeeman patterns of these $^2E$ and $^2T_1$ states would approach the linear behaviors $\mu_B(k M_L + 2 M_S)B$ with $k = 0.72$, $M_L = 2, 1, 0, -1, -2$, and $M_S = 1/2, -1/2$ [38].

The Zeeman patterns on ruby discussed above can be regarded as a kind of the PB effect. However, to the best of our knowledge, such PB effect has not been proposed for describing the crossover from the AZ effect to the NZ effect under the crystal-field splitting, possibly due to the lack of proper situation. The energy scale of the crystal field as well as the complexity of the level splittings or hybridizations make it challenging to clearly observe the crystal-field PB effect. Note that the magnetic field accessible by the current technology is at most $10^3 \sim 10^4$ T [42, 43]. Therefore, our experimental observation of the onset of the crystal-field PB effect at above 100 T owes to the accidental crystal-field splitting manner in ruby, i.e. the exceptionally small energy gap $\Delta$ between the $^2E$ and $^2T_1$ states of the $3d^3$ multiplets.

In conclusion, the AZ effect was observed for the R lines of ruby at above 100 T. The crystal-field multiplet theory with several empirical parameters successfully reproduces the experimental Zeeman patterns up to 230 T, proving that the hybridization with the second excited states are responsible for their nonlinear behaviors. Notably, the observed Zeeman patterns for $\mathbf{B} \perp c$ signal the crossover from one to another PB effect, characterized by the reconstruction of the good quantum number from only $M_S$ to both $M_L$ and $M_S$. The present work...
offers a new concept of the PB effect, which is distinct from the conventional PB effects describing atomic energy levels, and it could be universally encountered in crystal if the conditions are met.

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[18] See Supplemental Material at ??? for details of the experiment and theory.
[19] These values are different from those of the intercepts shown in Figs. 4(a)–4(h). This is because $|c|^{2}$ of each component changes discontinuously due to the lifting of degeneracy when a magnetic field is applied.
[20] The finite energy gap between the first and second excited states, $^{2}E$ and $^{2}T_{1}$, is attributed to the single-ion Coulomb interactions in the framework of the crystal-field theory. Three Kramers doublets originating from the $^{2}T_{1}$ states are represented as $^{2}T_{1}$, $^{2}E$, and $^{2}E$. In ruby, the main components contributing to each of the doublet are as follows: $|+\frac{1}{2}a_{1}^{*}$ and $|+\frac{1}{2}a_{2}^{*}$ for $^{2}E$, $|+\frac{1}{2}a_{1}^{*}$ and $|+\frac{1}{2}a_{2}^{*}$ for $^{2}E$, and $|+\frac{1}{2}a_{1}^{*}$ and $|+\frac{1}{2}a_{2}^{*}$ for $^{2}E$.
[21] Here, we assume $k = k' = 1$ because the covalent bonds could be broken in such high fields.