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Accumulated photon echo in ruby under hydrostatic pressure: Ground-state splitting and spontaneous decay of $2\bar{A}(^2E)$

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The technique of accumulated photon echo is used in combination with a high-pressure diamond anvil cell to measure the splitting of the 4A_2 ground state and the one-phonon spontaneous decay rate of the $2\bar{A}(^2E)$ level at 10 K in ruby up to 4.3 GPa of hydrostatic pressure. The 4A_2 ground-state splitting is found to be $0.383 \pm 0.001 \text{ cm}^{-1}$ at ambient pressure, and increases with a slope of $+(6 \pm 1) \times 10^{-3} \text{ cm}^{-1}/\text{GPa}$. The spontaneous decay rate of $2\bar{A}(^2E)$ increases only weakly with pressure. The pressure dependences of both quantities are accounted for in terms of the trigonal-field and spin-orbit-coupling parameters.

I. INTRODUCTION

The primary objective of this paper is to gain a better understanding of the trigonal-field and spin-orbit-coupling parameters of Cr^{3+} in ruby through the application of hydrostatic pressure. These parameters are accessible via the energy splittings resulting from fields of lower than cubic symmetry and from the spin-orbit coupling,^{1,2} particularly the splitting of the 4A_2 ground state. Cubic crystalline fields provide the gross features of the energy-level scheme of Cr^{3+} in ruby.³ Besides the pressure dependence of the 4A_2 splitting, we have measured the pressure dependence of the relaxation rate of the $2\bar{A}(^2E)$ state because it yields information on the diagonal elements of the trigonal field and spin-orbit coupling. The decay of $2\bar{A}(^2E)$ is caused by the transition to $\bar{E}(^2E)$ during the emission of a resonant phonon.⁴

Although the point-charge model has occasionally been successful in explaining the crystal-field parameters,⁵ it has become apparent that covalency is significant, if only by reason of the sizeable reduction of the spin-orbit coupling with respect to the free-ion value.^{6,7} Hydrostatic pressure presumably is the best means for examining these effects because it brings about a more or less isotropic compression of the ion's surroundings. The use of diamond anvil cells makes it possible to reach high hydrostatic pressures and allows optical access to the sample.⁸ This means that nonlinear-optical techniques can be extended to high-pressure spectroscopic studies.⁹ In the present case, an appropriate optical technique is the picosecond accumulated photon echo.¹⁰ The technique permits the measurement of the $2\bar{A}(^2E)$ relaxation rate in the time domain and of the 4A_2 splitting¹¹ in the frequency domain, despite the substantial pressure-

induced shifts and the substantial inhomogeneous broadening of the optical transitions concerned.

II. EXPERIMENTS

A. Experimental details

To reach high pressures, use was made of a standard diamond anvil cell,⁹ which basically consists of two anvil-shaped diamonds and a gasket in between, pressed together by means of a lever mechanism. The gasket, made of 0.5-mm-thick Inconel 740 sheet steel, was first indented to a thickness of 200 μm while mounted in the cell, after which a hole with a diameter of 200 μm was formed by means of spark erosion. Optical access to the sample was provided through the diamonds. The crystals used in the experiments, typically measuring $100 \times 100 \times 100 \mu\text{m}^3$, were cut from polished 700-at.ppm $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ platelets, and mounted in the cell with the c axis perpendicular to the cell axis. To ensure hydrostatic pressure, the compressed volume is filled with a 4:1 methanol-ethanol mixture¹²⁻¹⁴ or Ar (Ref. 15) as a pressure-transmitting medium. To suppress thermal phonons, the entire diamond anvil cell was cooled in a helium exchange cryostat, which reaches temperatures down to 10 K. The temperature was determined with a calibrated temperature-dependent resistor. The pressure was determined from the frequency of the R_1 luminescence in the standard way.¹⁶ The small width of the inhomogeneously broadened R_1 absorption line was testimony to the good hydrostatic conditions in the diamond anvil cell.¹²

In performing an accumulated photon echo,¹⁰ a train of optical pulse pairs is applied over the $^4A_2-\bar{E}(^2E)$ or the $^4A_2-2\bar{A}(^2E)$ transition. The first, or pump, pulse of

each pulse pair excites all Cr^{3+} centers in phase. The second, or probe, pulses are applied at a variable delay t_{12} after the first pulse. They further excite or deexcite the Cr^{3+} depending on t_{12} and the specific resonance frequency. Accumulated over the radiative lifetime ($\simeq 4$ ms), the train of pulse pairs results in a spectral-spatial grating with a spectral periodicity equal to $2\pi/t_{12}$, and a spatial periodicity determined by the angle between the pump and probe beams. Excitation by the pump pulse further leads to an echo of macroscopic polarization at the time of the probe pulse. Since the echo signal interferes with the probe pulse, the signal intensity scales linearly with the echo polarization. The decay rate of the echo thus is *double* the homogeneous dephasing rate, compared to four times in conventional two-pulse photon echo. In systems having a small enough splitting of one of the terminal levels of the optical transition, the accumulated echo intensity exhibits an additional oscillatory dependence on the delay.¹¹ The oscillatory dependence results from interference of the associated optical polarizations. In the present case, the beats occurring in the ${}^4A_2\text{-}\bar{E}({}^2E)$ and the ${}^4A_2\text{-}2\bar{A}({}^2E)$ echoes directly reflect the 4A_2 ground-state splitting. The optical field, of course, needs to be sufficiently intense in relation to the detunings of the two optical transitions departing from 4A_2 to allow their simultaneous coherent excitation.

A mode-locked Ar-ion laser operating at a pulse repetition frequency of 82 MHz is employed to pump synchronously a dye laser operating with 4-dicyanomethylene-2-methyl-6-*p*-dimethylaminostyryl-4*H*-pyran (DCM) dye. The dye laser produces Fourier-limited 10-ps pulses with a wavelength of 690 nm at a typical average output power of 40 mW. The beam of the dye laser is split into two beams of equal intensity. These beams are at a mutual angle of about 10° of arc, and focused to overlap at a single spot in the sample. A telescopic lens configuration here ensures a small focus. The second, or probe, pulse is delayed by up to a few nanoseconds by a scannable optical delay line.

The accumulated-photon-echo signal is detected by a photodiode as a change in the intensity of the probe pulse transmitted through the sample. The noise, which at low frequencies chiefly originates from the dye laser, levels off above a frequency of approximately 10 MHz. In order to improve the signal-to-noise ratio, therefore, we employed a double-modulation technique. The pump beam is modulated at 10 MHz by means of an electro-optical modulator, and the output of the photodiode passes through a narrow-band filter tuned to this frequency. The probe beam is modulated with a mechanical chopper at a frequency that is so low compared to the lifetime of the $\bar{E}({}^2E)$ bottleneck level (~ 60 Hz) that the grating and the associated accumulated-photon-echo signal disappear in the off period. The 10-MHz modulation is extracted from the background, and demodulated with an rf receiver.¹⁷ Finally, the audio-frequency signal is detected by means of a lock-in amplifier, the output of which is digitized for further processing. Decay curves are acquired by moni-

toring the output of the lock-in amplifier while scanning the delay between the pump and the probe beams with the optical delay line.

B. Results

As representative examples, the accumulated-photon-echo traces obtained at 4.3 GPa are presented in Fig. 1. An overall single-exponential decay, related to the homogeneous dephasing of the transition, along with an oscillatory behavior are observed. The latter, as already pointed out, reflects the zero-field ground-state splitting.¹¹ Added together, the accumulated photon echoes of the ${}^4A_2\text{-}2\bar{A}({}^2E)$ and the ${}^4A_2\text{-}\bar{E}({}^2E)$ transitions have the general form

$$I_{\text{echo}} \propto (1 + \alpha \cos \Delta t_{12}) e^{-2t_{12}/T_2}, \quad (1)$$

in which t_{12} is the delay, α measures the modulation depth, and Δ is the ground-state splitting. It is noted, however, that in the case of the ${}^4A_2\text{-}\bar{E}({}^2E)$ transition the decay is only marginal within the present time window. In the case of the ${}^4A_2\text{-}2\bar{A}({}^2E)$ transition, light that is polarized parallel or perpendicular to the *c* axis excites only one of the two ground-state components,¹⁸ with the result that no modulation is present. In Fig. 1, the polarization was adjusted for maximum absorption by the sample, in which case the polarization makes a finite angle with the *c* axis. A modulation is indeed observed for the echo of the ${}^4A_2\text{-}2\bar{A}({}^2E)$ transition.

FIG. 1. The accumulated-photon-echo intensity vs the delay for the ${}^4A_2\text{-}\bar{E}({}^2E)$ (upper frame) and ${}^4A_2\text{-}2\bar{A}({}^2E)$ (lower frame) transitions in ruby at a pressure of 4.3 GPa with Ar as the pressure-transmitting medium. The solid curves are fits to the data.

The results of the pressure dependence of the ground-state splitting are presented in Fig. 2. The results are derived from either the ${}^4A_2-\overline{E}({}^2E)$ or the ${}^4A_2-2\overline{A}({}^2E)$ transition. A linear increase in the ground-state splitting with increasing pressure is observed from the precision value $0.383 \pm 0.001 \text{ cm}^{-1}$ at ambient pressure¹¹ to $0.403 \pm 0.004 \text{ cm}^{-1}$ at 4.3 GPa. The ambient-pressure value was confirmed during the present experiment. From a fit to the data points, we find a slope of $+(6 \pm 1) \times 10^{-3} \text{ cm}^{-1}/\text{GPa}$. We note that this is comparable with the result $7 \times 10^{-3} \text{ cm}^{-1}/\text{GPa}$ obtained from experiments up to 0.6 GPa.¹⁹

Accumulated photon echo performed on the ${}^4A_2-2\overline{A}({}^2E)$ transition shows not only the oscillatory behavior associated with the ground-state splitting, but also a significant loss of coherence. The latter is to be attributed to the decay of $2\overline{A}({}^2E)$ to $\overline{E}({}^2E)$ during the emission of a resonant 29-cm^{-1} phonon. The associated lifetime T_1 of the $2\overline{A}({}^2E)$ level is related to the dephasing time T_2 by

$$T_1 = \frac{1}{2}T_2. \quad (2)$$

Equation (2) only applies if the dephasing is governed by lifetime decay. This condition is inferred to hold from the minor decay of the echo intensity observed for the ${}^4A_2-\overline{E}({}^2E)$ transition at ambient pressure in the present time window. Furthermore, no additional decay of the ${}^4A_2-\overline{E}({}^2E)$ echo intensity is observed upon applying pressure, which is indicative of the absence of significant inhomogeneous broadening of the ground-state splitting as well as negligible heating of the sample. The results for the relaxation rate T_1^{-1} as function of the pressure are shown in Fig. 3. An increase in the relaxation rate with increasing pressure is observed. The data point taken with the alcohol mixture as a pressure transmitting medium probably overestimates the relaxation rate because of nonhydrostatic contributions.

FIG. 2. The ground-state splitting in ruby as a function of the pressure (■ ambient pressure; ○ pressure transmission by a 4:1 methanol-ethanol mixture; ● pressure transmission by Ar). The straight line is a fit to the data.

FIG. 3. The one-phonon relaxation rate of $2\overline{A}({}^2E)$ to $\overline{E}({}^2E)$ in ruby as a function of the pressure (■ ambient pressure; ○ pressure transmission by a 4:1 methanol-ethanol mixture; ● pressure transmission by Ar). The solid line is the pressure dependence calculated as described in the text.

III. DISCUSSION

A. Trigonal field and spin-orbit coupling

The spectrum of substitutional Cr^{3+} in Al_2O_3 has been a subject of extensive theoretical study.^{1,2,18} Sugano and Tanabe¹⁸ were the first to consider the 4A_2 and 2E splittings, and concluded that they result from the combined action of the spin-orbit coupling and the trigonal distortion of the oxygen octahedra. Their calculation yielded a reasonable result for the 2E splitting, but the 4A_2 splitting was found to have the wrong sign. Later, the calculations for the 4A_2 splitting were refined by Sugano and Peter.¹ This yielded the correct sign as well as the correct order of magnitude. Eventually, both splittings were accounted for in detail by Macfarlane,² who demonstrated that, to third order of the perturbations, the leading terms in the splitting of 4A_2 read

$$\Delta = -2\sqrt{2}\zeta'^2 v' \left(\frac{2}{3D_1D_4} + \frac{1}{D_2D_3} + \frac{1}{D_2D_4} \right), \quad (3)$$

and that, to second order, the splitting of 2E equals

$$\delta = \frac{4\zeta v}{3D_7}. \quad (4)$$

Here, the quantities D_i occurring in the denominators are energy separations, which are specified in Table I along with their values and derivatives with respect to hydrostatic pressure, both at ambient pressure. The trigonal field is characterized by the semi-empirical parameters²⁰

$$v = -3\langle t_+ | V_{\text{trig}} | t_+ \rangle, \quad (5)$$

$$v' = \langle t_+ | V_{\text{trig}} | e_+ \rangle, \quad (6)$$

and the one-electron spin-orbit-coupling parameters ζ and ζ' are defined by¹

TABLE I. Energy denominators D_i in $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ and their linear shifts under hydrostatic pressure.

Denominator ^a	D_i (cm^{-1})	$\frac{dD_i}{dp}$ ($\text{cm}^{-1}/\text{GPa}$)
$D_1 = W(^4T_2) - W(^4A_2)$	18033 ^b	98 ^b
$D_2 = W(a^2T_2) - W(^4A_2)$	21139 ^b	1.8 ^b
$D_3 = W(b^2T_2) - W(^4A_2)$	33000 ^c	100 ^d
$D_4 = W(a^4T_1) - W(^4A_2)$	24767 ^b	104 ^b
$D_7 = W(a^2T_2) - W(a^2E)$	6734 ^b	9.4 ^b

^a $W(X)$ stands for the energy of level X in the notation of Ref. 2: $a^2T_2 \equiv t_2^2T_2$, $b^2T_2 \equiv t_2^2(^3T_1)e^2T_2$, $a^4T_1 \equiv t_2^2e^4T_1$, and $a^2E \equiv t_2^2E$.

^bTaken from Ref. 27.

^cEstimated from first-order crystal-field theory, which yields $D_3 = \Delta + 9B + 3C$.

^dThe cubic crystal field provides the major contribution to the pressure dependence of D_3 . The contributions of the Racah parameters B and C can be ignored on account of the small pressure dependence of the energy splittings within the t_2^3 configuration.

$$\zeta = -2\langle t_+ | V_{\text{s.o.}} | t_+ \rangle, \quad (7)$$

$$\zeta' = -\sqrt{2}\langle t_+ | V_{\text{s.o.}} | e_+ \rangle, \quad (8)$$

in which $|t_+\rangle$ and $|e_+\rangle$ are one-electron d wave functions in the cubic field. If the radial parts of $|t_+\rangle$ and $|e_+\rangle$ are identical, as they would be in the absence of covalency, we have $\zeta = \zeta'$ [cf. Eqs. (13) and (14) below].

Blume *et al.*⁴ showed that the ratio of the spontaneous spin-nonflip and spin-flip relaxation rates equals

$$\frac{w_{2\bar{A}_{\pm} \rightarrow \bar{E}_{\pm}}}{w_{2\bar{A}_{\pm} \rightarrow \bar{E}_{\mp}}} = 2 \left(\frac{v}{\zeta} \right)^2. \quad (9)$$

The spin-flip rate at ambient pressure is known to be 60 MHz.²¹ In a previous paper,¹¹ we determined the spin-nonflip relaxation rate at ambient pressure to be 1.4 GHz. When we insert these two rates into Eq. (9) to obtain v/ζ , and subsequently combine this result with ζv derived from the 2E splitting [Eq. (4)], we arrive at the values for v and ζ entered in Table II. Note that both the relaxation rates and the splitting of 2E are due to admixture of the 2T_2 level. Macfarlane,²² using another scheme, derived numerical values for v and v' from the dependences of the quartet-level band splittings on the trigonal-field parameters, and alternatively from the dependences of the 2T_1 and 2T_2 splittings. The quartet level splittings were best described by $v \simeq 800 \text{ cm}^{-1}$ and $v' \simeq 400 \text{ cm}^{-1}$. The splittings of the 2T_1 and 2T_2 levels were best fitted with $v \simeq 800 \text{ cm}^{-1}$ and $v' \simeq 680 \text{ cm}^{-1}$. The latter value for v' should be given a heavier weight, since the 2T_1 and 2T_2 splittings are more accurately determined than those of the quartet levels. Noting that the precise value of v' is of minor concern for the results

TABLE II. Values at ambient pressure and pressure dependences of trigonal-field and spin-orbit-coupling parameters in $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$.

X	X_0 (cm^{-1})	$\frac{1}{X_0} \frac{dX}{dp}$ (10^{-3} GPa^{-1})
v	711 ^a	+8 ^b
v'	600 ^c	+6 ^b
ζ	206 ^a	-8
ζ'	215 ^d	+7

^aCalculated from the ratio of spin-nonflip and spin-flip relaxation rates.

^bFrom Eqs. (10) and (11) and the observed pressure dependence of R (Refs. 24 and 25).

^cEstimated from band splittings (Ref. 2).

^dCalculated from the ground-state splitting.

presented here, we adopt $v' = 600 \text{ cm}^{-1}$. Combining this value of v' with Eq. (3) subsequently yields a value for ζ' . The results are summarized in Table II.

To estimate the pressure dependences of the trigonal-field parameters, we rely on the point-charge expressions derived by McClure.²³ He showed that the trigonal-field parameters can be written as

$$v = b_2 \langle r^2 \rangle + b_4 \langle r^4 \rangle, \quad (10)$$

$$v' = -\frac{1}{3} \sqrt{2} b_2 \langle r^2 \rangle + \frac{1}{4} \sqrt{2} b_4 \langle r^4 \rangle, \quad (11)$$

where $\langle r^2 \rangle$ and $\langle r^4 \rangle$ are the expectation values of r^2 and r^4 over the radial part of the one-electron d wave function. The parameters b_2 and b_4 , which depend on the position of the ligand ions, are liable to considerable uncertainty, both in sign and magnitude (see Table VI of Ref. 23). Therefore, the best approach is to derive b_2 and b_4 at ambient pressure from the empirical v and v' . With regard to the pressure dependences of b_2 and b_4 , it has been shown that in good approximation the ruby structure is uniformly compressed under hydrostatic pressure. In particular the c/a ratio turned out to be insensitive to hydrostatic pressure.^{24,25} The major contribution to the pressure dependence of the trigonal field then presumably stems from the change of the interatomic distances. In spite of a certain amount of covalency, this dependence is reasonably well described by the point charge model. That is,

$$b_i \propto \frac{1}{R^{i+1}}, \quad (12)$$

in which R represents the interatomic distances. Calculations on the basis of Eqs. (10), (11), and (12) using the empirical values of b_2 and b_4 at ambient pressure and the measured pressure dependence of R (Refs. 24 and 25) predict, as anticipated, a rise of the trigonal-field parameters with increasing pressure by a fraction of a percent per GPa (Table II). Here, values for $\langle r^2 \rangle$ and

$\langle r^4 \rangle$ are taken from Ref. 26. In the range of v' of interest ($v' \sim 600 \text{ cm}^{-1}$), the increase in v and v' depends only weakly on the precise value adopted for v' . The results for the pressure dependences of v and v' (Table II) are estimated to be accurate to about 30%.

To determine the pressure dependence of the spin-orbit-coupling parameter ζ , we rely on the pressure dependence of the 2E splitting as measured from the separation of the R lines. Data up to 20 GPa indicate that the 2E splitting decreases with a fractional slope of $1.7 \times 10^{-3} \text{ GPa}^{-1}$.¹⁴ [The $2\bar{A}({}^2E) - \bar{E}({}^2E)$ splitting was found to rise beyond 40 GPa.⁸] Inserting this dependence into Eq. (4) together with the pressure dependence of v just derived and the pressure dependence of D_7 (Table I),²⁷ we find that ζ decreases by $8 \times 10^{-3} \text{ GPa}^{-1}$. For the pressure dependence of ζ' we turn to the ground-state splitting in a similar procedure using the pressure dependence as measured here from accumulated photon echo (Fig. 2). Inserting the pressure dependence of v' (Table II) together with the minor pressure dependences of the relevant D_i ($i = 1, 2, 3, 4$), we then arrive at a relative increase in ζ' amounting to $+7 \times 10^{-3} \text{ GPa}^{-1}$. In consideration of the approximations made, this result is again accurate to about 30%. The important point to note, however, is that ζ' definitely increases with pressure, whereas ζ decreases.

To make this plausible, we refer to the work of Sugano, Tanabe, and Kamimura²⁸ who showed that, upon neglect of all contributions of order higher than quadratic, the spin-orbit-coupling parameters are given by

$$\zeta \approx [1 + (S_\pi^2 - \gamma_\pi^2)]\zeta_d + \frac{1}{2}\lambda_\pi^2\zeta_{Lp}, \quad (13)$$

$$\zeta' \approx [1 + \frac{1}{2}(S_s^2 - \gamma_s^2) + \frac{1}{2}(S_\sigma^2 - \gamma_\sigma^2) + \frac{1}{2}(S_\pi^2 - \gamma_\pi^2)]\zeta_d - \frac{1}{2}\lambda_\sigma\lambda_\pi\zeta_{Lp}, \quad (14)$$

where ζ_d and ζ_{Lp} are the free-ion values of the spin-orbit-coupling parameters of the metal-ion d orbital and the ligand p orbital, respectively. The quantities S_i ($i = s, \sigma, \pi$) are the overlap integrals between the metal-ion orbitals and the ligand orbitals. The parameters γ_i measure the amount of covalency, indicating the admixture of metal-ion orbitals into the bonding molecular orbitals of mainly ligand character, and similarly the λ_i specify the admixture of the ligand orbitals into the antibonding molecular orbitals of mainly metal-ion character. We have $\lambda_i = (\gamma_i + S_i)/(1 + \gamma_i S_i)$. The fact that ζ is substantially smaller than the free-ion value $\zeta_d = 292 \text{ cm}^{-1}$ (Ref. 29) indicates that the covalency parameters exceed the overlap integrals, at least for the π -bonding molecular orbitals. Note that ζ_{Lp} is of the order of 120 cm^{-1} ,³⁰ so that the effects of the last terms in Eqs. (13) and (14) may be ignored in a discussion of the major mechanisms leading to the pressure dependence. The overlap integral S_π is indeed small, since the relevant atomic and ligand orbitals point *away* from the bond. Conversely, atomic and ligand orbitals point *towards* each other along the

bond in the case of σ bonding, so that S_σ is relatively large. When putting ruby under hydrostatic pressure, we accordingly expect S_σ to grow much faster than S_π . As for ζ , the increment of S_π is obviously overcompensated by an increase in the covalency parameter associated with the π -bonding orbital, with the result that ζ decreases with pressure. In the case of ζ' , by contrast, the increase in S_σ with pressure apparently overshadows all of the effects on the covalency parameters to such an extent that ζ' rises by an amount similar to the decrement of ζ .

B. Spin-nonflip phonon relaxation rate

We now turn to a discussion of the pressure dependence of the relaxation of $2\bar{A}({}^2E)$. The relaxation is dominated by the spin-nonflip decay to $\bar{E}({}^2E)$, with a correction of order 5% resulting from spin-flip decay. Blume *et al.*⁴ have calculated the spin-flip relaxation rate from $2\bar{A}({}^2E)$ to $\bar{E}({}^2E)$, with the result

$$w_{2\bar{A}\pm \rightarrow \bar{E}\mp} = \frac{27}{4} \left(\frac{\Delta E}{T_{z'z'}} \frac{1}{S_{33} - S_{13}} \right)^2 \times \frac{\delta^3}{135\pi\rho\hbar^4} \left(\frac{1}{v_t^5} + \frac{3}{2v_l^5} \right) (n+1), \quad (15)$$

Here, ΔE is the change in the spacing δ between $2\bar{A}({}^2E)$ and $\bar{E}({}^2E)$ invoked by a stress $T_{z'z'}$, applied along the [111] direction of the octahedron, S_{13} and S_{33} are elastic compliance constants, ρ is the mass density of the crystal, v_t and v_l are the transverse and longitudinal sound velocities, and n is the phonon occupation number. From Eq. (15), the spin-nonflip rate $w = w_{2\bar{A}\pm \rightarrow \bar{E}\pm}$ can in turn be deduced with the help of their result for the ratio of the spin-nonflip and spin-flip rates [Eq. (9)]. The quantity n is set to zero, since the temperature is well below that corresponding to the 2E splitting ($\delta/k_B \approx 40 \text{ K}$).

The dependences on hydrostatic pressure of the various parameters determining the relaxation as well as their fractional contributions to the pressure dependence of w are listed in Table III. The mass density scales with the inverse of the crystal volume, whose dependence on hydrostatic pressure has been measured in the pressure range of interest with x-ray diffraction.^{24,25} The variation in the sound velocities has been determined straightforwardly with ultrasound measurements.³¹ The variation in the 2E splitting is derived by us from the position of the R_1 and R_2 luminescences under hydrostatic pressure.¹⁴ The variation of the elastic constants can be estimated from the pressure dependences of the sound velocity, and the mass density by use of relations of the form $v = (\rho S)^{-1/2}$. Assuming all elastic constants to vary by the same fraction, we then arrive at the estimate for their pressure dependence given in Table III. The effects of the parameters v and ζ are inserted in Table III in conformity with the results in Table II.

The factor in the relaxation rate remaining to be considered, therefore, is the combination $\Delta E/T_{z'z'}$, i.e., the change in the 2E splitting per unit of stress along the c

TABLE III. The dependence on hydrostatic pressure of the parameters X occurring in Eqs. (9) and (15), and their fractional contributions to the spin-nonflip $2\bar{A}(^2E)$ relaxation rate w .

X	$\frac{1}{X_0} \frac{dX}{dp}$ (10^{-3} GPa^{-1})	$\frac{1}{w_0} \frac{\partial w}{\partial X} \frac{dX}{dp}$ (10^{-3} GPa^{-1})
ρ	$+4^a$	-4
v_l, v_t	$+3.46^b$	-17.3
δ	-1.7^c	-5.1
S_{13}, S_{33}	-11^d	$+22$
$\Delta E/T_{z'z'}$	e	
v	$+8^f$	$+16$
ζ	-8^f	$+16$
Total		$+28 \pm 10$
Experiment		$+55 \pm 30$

^aDerived from the change in volume (Refs. 24 and 25).

^bFrom ultrasound measurements (Ref. 31).

^cDerived from luminescence data (Ref. 14).

^dCalculated from the dependence of the speed of sound on the elastic constants and the mass density. The elastic constants are assumed to vary equally with pressure. The pressure dependence of the speed of sound is taken from Ref. 31.

^eEstimated to be small.

^fTaken from Table II.

axis. This quantity occurs in Eq. (15) because it is a measure of the coupling of the two-level system with the lattice vibrations. Whereas reliable values are available for the magnitude of $\Delta E/T_{z'z'}$,³² its variation with hydrostatic pressure is not known, nor can it be related to measured pressure dependences of suitable quantities from other sources. Some insight may, however, be gained by differentiating δ with respect to $T_{z'z'}$. Converting $T_{z'z'}$ to the stress-induced strain e via relationships of the form $e = TS$, we then find from Eq. (4)

$$\frac{\Delta E}{T_{z'z'}} = \frac{d\delta}{dT_{z'z'}} = \frac{4S}{3D_7} \left(\frac{d\zeta}{de} v + \zeta \frac{dv}{de} \right). \quad (16)$$

In Eq. (16), S/D_7 and ζ are known to decrease with

hydrostatic pressure, while v increases. With regard to dv/de , on the grounds of the steep dependence of v on the interatomic distances it is reasonable to assume that its absolute value increases upon compression of the lattice [cf. Eq. (12)]. A similar reasoning probably applies to $d\zeta/de$. All of these effects added together lead to the conjecture that the dependence of $\Delta E/T_{z'z'}$ on hydrostatic pressure is indeed weak.

When using the pressure dependences as summarized in Table III, we see that the effects of all pressure dependences on the relaxation rate except that of $\Delta E/T_{z'z'}$ add up to $+28 \times 10^{-3} \text{ GPa}^{-1}$, which in Fig. 3 is represented by the solid line. This result has an estimated uncertainty of $\pm 10 \times 10^{-3} \text{ GPa}^{-1}$, residing primarily in the pressure dependences of v and ζ . In any case, however, the calculations suggest that the relaxation rate rises with hydrostatic pressure. This is found to be verified by the data in Fig. 3, which correspond to a relative slope of $+(55 \pm 30) \times 10^{-3} \text{ GPa}^{-1}$. The conformity, incidentally, also substantiates the conclusion arrived at for $\Delta E/T_{z'z'}$.

IV. CONCLUSIONS

We have demonstrated the feasibility of combining the technique of accumulated photon echo, a powerful tool for measuring optical dephasing of electronic centers and small level splittings in solids, with the diamond anvil cell, which is capable of achieving high hydrostatic pressures. We have used this combination to measure the 4A_2 ground-state splitting and the $2\bar{A}(^2E)$ one-phonon spin-nonflip relaxation rate in ruby as a function of hydrostatic pressure up to 4.3 GPa. The pressure dependences of both quantities can be adequately interpreted in terms of the pressure dependences of the trigonal-field and the spin-orbit-coupling parameters.

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