Magnons and Magnetodielectric Effects in CoCr$_2$O$_4$: Raman Scattering Studies

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Magnetoelcetric materials have generated wide technological and scientific interest because of the rich phenomena these materials exhibit, including the coexistence of magnetic and ferroelectric orders, magnetoelcetric behavior, and exotic hybrid excitations such as electromagnons. The multiferroic spinel material, CoCr$_2$O$_4$, is a particularly interesting example of a multiferroic material, because evidence for magnetoelectric behavior in the ferrimagnetic phase seems to conflict with traditional noncollinear-spin-driven mechanisms for inducing a macroscopic polarization. This paper reports an inelastic light scattering study of the magnon and phonon spectrum of CoCr$_2$O$_4$ as a function of temperature, pressure, and magnetic field. Below the Curie temperature ($T_C \sim 94$ K) of CoCr$_2$O$_4$ we observe a $Q \sim 16$ cm$^{-1}$ $q = 0$ magnon having $T_{1g}$-symmetry, which has the transformation properties of an axial vector. The anomalously large Raman intensity of the $T_{1g}$-symmetry magnon is characteristic of materials with a large magneto-optical response and likely arises from large magnetic fluctuations that strongly modulate the dielectric response in CoCr$_2$O$_4$. The Raman susceptibility of the $T_{1g}$-symmetry magnon exhibits a strong magnetic-field dependence that is consistent with the magnetodielectric response observed in CoCr$_2$O$_4$, suggesting that magnetodielectric behavior in CoCr$_2$O$_4$ primarily arises from the field-dependent suppression of magnetic fluctuations that are strongly coupled to long-wavelength phonons. Increasing the magnetic anisotropy in CoCr$_2$O$_4$ with applied pressure decreases the magnetic field-dependence of the $T_{1g}$-symmetry magnon Raman susceptibility in CoCr$_2$O$_4$, suggesting that strain can be used to control the magnetodielectric response in CoCr$_2$O$_4$.

I. INTRODUCTION

Multiferroics—materials exhibiting a coexistence of both magnetic and ferroelectric orders$^{1,2}$—have attracted substantial technological and scientific interest recently. The technological interest stems from the multifunctional properties exhibited by multiferroics, which make them potentially useful in device applications such as magnetoelcetric memories and switches. Multiferroics are scientifically interesting, in part, because they exhibit a variety of microscopic mechanisms that can result in an interesting interplay between ferroelectric and magnetic orders; among other consequences, this interplay can spawn interesting dynamical properties in multiferroic materials, including electromagnons, i.e., hybrid excitations involving a coupling between optical phonons and spin waves via the magnetoelectric interaction$^{3-14}$ and magnetodielectric effects.$^{15-17}$

Materials in which geometric frustration leads to non-collinear spin order and strong spin-lattice coupling are particularly rich material environments to find novel magnetoelectric behavior.$^{1,18}$ Transition-metal-oxide spinel materials (AB$_2$O$_4$), for example, exhibit both non-collinear spin orders and strong spin-lattice coupling that can lead to magnetoelectric coupling, because the presence of magnetic ions on the $B$-site pyrochlore lattice of the spinel structure often leads to strong geometric frustration and consequent non-collinear orders that can generate multiferroic phenomena.$^5$ Magnetoelectric effects are indeed realized in some ACr$_2$O$_4$ spinels (e.g., A=Co$^{2+}$ and Fe$^{2+}$), in which the competition among the various exchange interactions, $J_{A-A}$, $J_{A-Cr}$, and $J_{Cr-Cr}$, involving the $A^{2+}$ ions and the $Cr^{3+}$ $S = 3/2$ spins lead to complex magnetic orders.$^{19,20}$

CoCr$_2$O$_4$, in particular, exhibits a succession of magnetic orders, including ferrimagnetic order below $T_C \sim 94$ K, incommensurate conical spiral order below $T_S \sim 26$ K, commensurate order below $T_L \sim 14$ K.$^{21,22}$ as well as spin-driven multiferroic behavior and dielectric anomalies below $T_S$.$^{23-25}$ Yet, the nature and origin of magnetodielectric behavior in CoCr$_2$O$_4$ remains uncertain. Multiferroicity in CoCr$_2$O$_4$ has been associated with the spin-current mechanism$^{26}$ involving cycloidal spin order.$^{23}$ in which the induced electric polarization is generated by the non-collinear spins$^{27}$ via the inverse Dzyaloshinskii-Moriya interaction, $P \sim e_B \times (S_i \times S_j)$. However, evidence for multiferroicity.$^{17,28}$ structural distortion,$^{17}$ and magnetodielectric behavior$^{17}$ have also been reported above $T_S$ in the ferrimagnetic state of CoCr$_2$O$_4$, raising questions about the origin of multiferroic behavior in this material. Yang et al., for example, have suggested that magnetodielectric behavior in CoCr$_2$O$_4$ results from the presence of multiferroic domains that are reoriented in the presence of a magnetic field.$^{17}$ But magnetodielectric behavior in magnetic materials can also arise from magnetic fluctuations that induce shifts in optical phonon frequencies via strong spin-lattice coupling.$^{16}$

Unfortunately, a lack of microscopic information regarding spin-lattice coupling has prevented a clear identi-
Raman intensity in CoCr$_2$O$_4$ has been observed in CoCr$_2$O$_4$ using infrared and terahertz spectroscopies and optical phonons in CoCr$_2$O$_4$ have been identified using Raman scattering and optical absorption measurements. However, to our knowledge, there have been no microscopic studies of spin-lattice coupling in CoCr$_2$O$_4$ that could clarify the origin of magnetodielectric behavior in this material. The application of pressure would be a useful means of studying spin-lattice coupling and its role in magnetoelectric behavior in spinels such as CoCr$_2$O$_4$; indeed, ab initio calculations predict that pressure should enhance the macroscopic polarization in the multiferroic regime of CoCr$_2$O$_4$. However, the effects of pressure on the magnetoelectric behavior and spin-lattice coupling in CoCr$_2$O$_4$ have not yet been experimentally investigated.

Raman scattering is a powerful tool for studying magnons, strong spin-lattice coupling and electromagnons in complex oxide materials. When used in conjunction with pressure and magnetic-field tuning, Raman scattering can provide pressure- and magnetic-field-dependent information about the energy and lifetime of phonons, magnons, and spin-phonon coupling effects. In this paper, we report an inelastic light (Raman) scattering study of magnon and phonon excitations in CoCr$_2$O$_4$ as simultaneous functions of temperature, pressure, and magnetic field. Below $T_C = 94$ K, we report the development in CoCr$_2$O$_4$ of a ~16 cm$^{-1}$ (2 meV) $q = 0$ magnon excitation with $T_{1g}$ symmetry. The anomalously large Raman scattering susceptibility associated with the $T_{1g}$ symmetry magnon in CoCr$_2$O$_4$ is indicative of a large magneto-optical response arising from large magnetic fluctuations that couple strongly to the dielectric response; this coupling is likely associated with the dielectric anomalies observed in the ferrimagnetic phase of CoCr$_2$O$_4$. We also show that the Raman intensity of the $T_{1g}$-symmetry magnon in CoCr$_2$O$_4$ exhibits a strong suppression with increasing magnetic field, suggesting that the dramatic magneto-dielectric behavior observed in CoCr$_2$O$_4$ results from the magnetic-field-induced suppression of magnetic fluctuations that are strongly coupled to phonons. Using applied pressure to increase the magnetic anisotropy in CoCr$_2$O$_4$ results in a decreased magnetic field-dependence of the $T_{1g}$-symmetry magnon Raman intensity in CoCr$_2$O$_4$, suggesting that pressure or epitaxial strain can be used to control magnetodielectric behavior and the magneto-optical response in CoCr$_2$O$_4$ by suppressing magnetic fluctuations.

II. EXPERIMENTAL METHODS

A. Crystal Growth and Characterization

CoCr$_2$O$_4$ crystals were grown by chemical vapor transport (CVT) following a procedure described by Ohgushi et al. Polycrystalline powder samples of CoCr$_2$O$_4$ were first synthesized using cobalt nitrate hexahydrate (Strem Chemicals 99%) and chromium nitrate nonahydrate (Acros 99%). The nitrates were combined in stoichiometric amounts and dissolved in water. The solution was heated to 350°C and stirred using a magnetic stir bar at 300 rpm until all of the liquid evaporated. The remaining powder was heated in an alumina crucible at 900°C for 16 hours and then air quenched. Crystalline samples of CoCr$_2$O$_4$ were grown by CVT using CrCl$_3$ as a transport agent. 2.0 g of polycrystalline samples and 0.04 g of CrCl$_3$ were sealed in an evacuated quartz ampoule, which was placed inside a three-zone furnace having 950°C at the center with a temperature gradient of 10°C/cm for one month. Crystals with typical dimensions of $2 \times 2 \times 2$ mm$^3$ were obtained.

The CoCr$_2$O$_4$ crystals were characterised using x-ray diffraction and magnetization measurements. Crystals of CoCr$_2$O$_4$ were ground to a powder to obtain the x-ray diffraction pattern using a Siemens-Bruker D5000 diffractometer using Cu-Kα radiation shown in Fig. 1. Rietveld refinement of the CoCr$_2$O$_4$ cell to the XRD data was performed using XND Rietveld, and indicates a pure sample with $Fd3m$ symmetry and a lattice constant of 8.334(1)Å, which agrees with the established structure. The $< 110>$ reflections from a single crystal of CoCr$_2$O$_4$ were measured, and no evidence of twinning imperfections was found. The field-cooled dc magnetization data on the CoCr$_2$O$_4$ powder from which our crystal sample was obtained was collected using a Quantum Design MPMS-3 and is shown as a function of temperature in Fig. 2. Our results are similar to existing data. In particular, the sudden increase in the molar susceptibility, $\chi_m$ at $T \sim 94$ K marks the onset of ferrimagnetic...
ordering. The change in slope of the graph at $T \sim 26$ K and an additional small anomaly at $T \sim 14$ K correspond to the incommensurate and commensurate spiral ordering, respectively, in CoCr$_2$O$_4$.

B. Raman Scattering Measurements

Raman scattering measurements were performed using the 647.1 nm excitation line from a Kr$^+$ laser. The incident laser power was limited to $5 - 10$ mW, and was focused to a $\sim 50$ µm-diameter spot to minimize laser heating of the sample. Sample heating by the laser was estimated to be in the range $5 - 7$ K, and this estimated laser heating is included in the temperatures given in the results section. The scattered light from the samples was collected in a backscattering geometry, dispersed through a triple stage spectrometer, and then detected with a liquid-nitrogen-cooled CCD detector. The samples were inserted into a continuous He-flow cryostat, which was horizontally mounted in the open bore of a superconducting magnet. This experimental arrangement allows Raman scattering measurements under the simultaneous conditions of low temperature ($3 - 300$ K), high magnetic fields ($0 - 9$ T), and high pressures ($0 - 100$ kbar). To determine the symmetries of the measured Raman excitations in zero magnetic field, linearly polarized incident and scattered light were used for various crystallographic orientations of the sample. In the magnetic field measurements, circularly polarized light was used to avoid Faraday rotation of the light polarization.

Magnetic field measurements were performed in both Voigt ($\mathbf{k} \perp \mathbf{M} \parallel \mathbf{H}$) and Faraday ($\mathbf{k} \parallel \mathbf{M} \parallel \mathbf{H}$) geometries, where $\mathbf{k}$ is the wavevector of the incident light and $\mathbf{M}$ is the magnetization direction. Because of the very small anisotropy field in CoCr$_2$O$_4$ ($H_A \leq 0.1$ T), the net magnetization $\mathbf{M}$ was assumed to follow the applied field $\mathbf{H}$ in all experiments performed. To verify this, we confirmed that the field-dependence of the Raman spectrum was independent of the crystallographic orientation of the applied field. The field measurements in the Faraday geometry were performed by mounting the sample at the end of the insert, as illustrated in Fig. 3(a), so that the wavevector of the incident light is parallel to the applied field. The Voigt geometry was achieved by mounting the sample on an octagon plate, which was mounted sideways on the sample rod, as illustrated in Fig. 3(b). The incident light was guided to the sample surface with a 45° mirror mounted on the sample rod. This sample mounting arrangement allows the magnetic field to be applied perpendicular to the wavevector of the incident light, $\mathbf{k} \perp \mathbf{M} \parallel \mathbf{H}$.

High pressure measurements were performed using a miniature cryogenic diamond anvil cell (MCDAC) to exert pressure on the sample via an argon liquid medium. The high-pressure cell was inserted into the cryostat as illustrated in Fig. 3(c), allowing the pressure to be changed in situ at low temperatures without any extra warm-
III. TEMPERATURE DEPENDENCE OF THE MAGNETIC EXCITATION AT \( P=0 \) AND \( B=0 \)

A. Results

Fig. 4 shows the \( T=10\) K and \( T=130\) K Raman spectra of CoCr\(_2\)O\(_4\) between 0-700 cm\(^{-1}\) in a scattering geometry with circularly polarized incident light and unanalyzed scattered light. The \( T=10\) K spectrum exhibits the five Raman-active phonon modes expected and previously observed\(^{\text{30–32}}\) for CoCr\(_2\)O\(_4\), including phonon modes at 199 cm\(^{-1}\), 454 cm\(^{-1}\), 518 cm\(^{-1}\), 609 cm\(^{-1}\), and 692 cm\(^{-1}\) (at \( T=10\) K). In addition to the phonon modes, the \( T=10\) K spectrum in Fig. 4 has an additional mode that develops near 16 cm\(^{-1}\) (~2 meV) below \( T=90\) K. The inset of Fig. 4 shows that the 16 cm\(^{-1}\) mode intensity is present only in the “depolarized” scattering geometry, i.e., only when the incident and scattered light polarizations are perpendicular to one another, independent of the crystallographic orientation. This polarization dependence indicates that the 16 cm\(^{-1}\) mode symmetry transforms like the fully antisymmetric representation, \( T_{1g} \), which has the symmetry properties of an axial vector, characteristic of a magnetic excitation.\(^{\text{47,48}}\) Consequently, we identify the 16 cm\(^{-1}\) excitation as a \( q=0 \) \( T_{1g} \) symmetry magnon in CoCr\(_2\)O\(_4\). This interpretation is supported by the temperature-dependence of the 16 cm\(^{-1}\) \( T_{1g} \)-symmetry mode Raman scattering susceptibility, \( \text{Im} \chi(\omega) \) (see Fig. 5(a)), where \( \text{Im} \chi(\omega) = S(q=0,\omega)/[1+n(\omega,T)] \), \( S(q=0,\omega) \) is the measured Raman scattering response, and \( [1+n(\omega,T)] \) is the Bose thermal factor with \( n(\omega,T) = [\exp(\hbar\omega/k_BT) - 1]^{-1} \). Fig. 5(b) shows that the \( \sim 16\) cm\(^{-1}\) \( T_{1g} \) symmetry mode energy (solid squares) decreases in energy (“softens”) with increasing temperature toward \( T_C \) —consistent with the temperature-dependence of the \( \text{Co}^{2+} \) sublattice magnetization\(^{\text{29}}\)—indicative of a single-magnon excitation.\(^{\text{47}}\) Fig. 5(b) also shows that the amplitude of the Raman susceptibility, \( \text{Im} \chi(\omega) \), associated with the 16 cm\(^{-1}\) \( T_{1g} \) symmetry magnon mode (solid circles) is relatively insensitive to temperature and is comparable to that of the 199 cm\(^{-1}\) \( T_{2g} \) phonon. Notably, the 16 cm\(^{-1}\) \( T_{1g} \) symmetry magnon we observe in CoCr\(_2\)O\(_4\) has a similar energy and temperature dependence to that of the exchange magnon observed previously in terahertz\(^{\text{28}}\) and infrared spectroscopy\(^{\text{29}}\) measurements of CoCr\(_2\)O\(_4\). Nevertheless, it is unlikely that the 16 cm\(^{-1}\) \( T_{1g} \) symmetry magnon we observe in CoCr\(_2\)O\(_4\) is the same as the intersublattice exchange mode reported in infrared measurements, because \( T_{1g} \) is not an infrared-active symmetry. Note in this regard that the spinel structure of CoCr\(_2\)O\(_4\) is expected to exhibit six \( q=0 \) magnon modes with 5 closely spaced optical branches,\(^{\text{28,49–51}}\) so we are likely observing a different optical magnon that is close in energy to that observed in infrared measurements.\(^{\text{28,29}}\)

B. Discussion and Analysis

The finite \( q=0 \) energy of the \( \omega \sim 16 \) cm\(^{-1}\) (2 meV) \( T_{1g} \)-symmetry magnon in CoCr\(_2\)O\(_4\) primarily reflects the finite exchange, \( H_E \), and anisotropy, \( H_A \), fields in CoCr\(_2\)O\(_4\), according to \( \omega = \gamma(2H_AH_E + H_A^2)^{1/2} \), where \( \gamma \) is the gyromagnetic ratio \( g\mu_B/\hbar \).\(^{\text{18}}\) Fig. 5 also shows that the 16 cm\(^{-1}\) \( T_{1g} \) symmetry magnon in CoCr\(_2\)O\(_4\) is apparent to temperatures as high as \( T \sim 60 \) K, indicating that the \( T_{1g} \) symmetry magnon in CoCr\(_2\)O\(_4\) is dominated by the \( \text{Co}^{2+} \) sublattice spins, which order at a significantly higher temperature (94 K) than the \( \text{Cr}^{3+} \) sublattice (49 K).\(^{\text{29}}\)

Importantly, the Raman susceptibility of the 16 cm\(^{-1}\) \( T_{1g} \) symmetry magnon at \( T=10 \) K (for \( H = 0 \) T and \( P = 0 \) kbar) (see Fig. 5) reflects the degree to which this magnon modulates the dielectric response, \( \epsilon = 4\pi\chi_E \) (where \( \chi_E \) is the electric susceptibility).\(^{\text{32,33}}\) Consequently, while Raman scattering from magnons is generally much weaker than Raman scattering from phonons,\(^{\text{47}}\) Figs. 4 and 5 show that Raman intensity of
the T_{1g}-symmetry magnon is comparable to that of the Raman-active phonons in CoCr$_2$O$_4$, indicative of a strong influence of this magnon on the dielectric response of CoCr$_2$O$_4$.

The large Raman susceptibility of the T$_{1g}$ symmetry magnon reflects a large magneto-optical response in CoCr$_2$O$_4$, and is likely associated with strong magnetic fluctuations that modulate the dielectric response via strong spin-lattice coupling. Such large magnetic fluctuations are attributable to the weak anisotropy field in CoCr$_2$O$_4$, $H_A \lesssim 0.1$ T, and can contribute in several ways to fluctuations in the dielectric response.

\[
\delta \epsilon(m,l) = i f \delta m + g(\delta l)^2 + a(\delta m)^2
\]

where $\delta \epsilon$ is the dielectric response fluctuation, $\delta m$ represents longitudinal fluctuations in the magnetization, $\delta l$ represents fluctuations of the antiferromagnetic vector, and $a$, $f$, and $g$ are constants. The first term in Eq. (1) is associated with the linear magneto-optical Faraday effect, the second term is associated with linear magnetic birefringence, and the final term is an isotropic "exchange" mechanism for magnon scattering that is present in non-collinear antiferromagnets. In non-collinear antiferromagnetic and ferrimagnetic materials with weak anisotropy—such as CoCr$_2$O$_4$—strong single-magnon scattering can result from large fluctuations of both $l$ and $m$. In particular, the one-magnon Raman scattering intensity, $S$, associated with large magnetic fluctuations of the antiferromagnetic vector at $H = 0$ is limited only by the anisotropy field, $H_A$ (i.e., $S \propto 1/H_A$), which is very small in CoCr$_2$O$_4$, $H_A \lesssim 0.1$ T.

**IV. MAGNETIC-FIELD-DEPENDENCE OF THE T$_{1g}$-SYMMETRY MAGNON IN CoCr$_2$O$_4$**

A. Results

Fig. 6 shows the magnetic-field-dependence of the Raman susceptibility, $\text{Im} \chi(\omega)$, for the T$_{1g}$-symmetry magnon of CoCr$_2$O$_4$ at $T = 10$ K with an applied magnetic field in both the (Fig. 6(a)) Faraday ($k \parallel M \parallel H$) and the (Fig. 6(b)) Voigt ($k \perp M \perp H$) geometries. Fig. 6(c) summarizes the field-dependences of the T$_{1g}$-symmetry magnon energy for CoCr$_2$O$_4$ at $T = 10$ K. This ratio is close to the $T = 4$
K value of $\hbar \omega / \mu_B H = 2.5$ is measured for the exchange magnon in CoCr$_2$O$_4$.\textsuperscript{29} and is consistent with the gyromagnetic ratio of 2.2 for Co$^{2+}$.\textsuperscript{28,57} Fig. 6(d) compares the field-dependence of the normalized $T_{1g}$-symmetry magnon intensity, $\text{Im} \chi_{mag}(\omega)/\text{Im} \chi_{ph}(\omega)$, in both the (filled circle and square) Faraday ($k \parallel M \parallel H$) and (filled triangle) Voigt ($k \perp M \parallel H$) geometries, where $\text{Im} \chi_{mag}(\omega)$ and $\text{Im} \chi_{ph}(\omega)$ are the Raman susceptibilities of the $T_{1g}$-symmetry magnon and 199 cm$^{-1}$ $T_{2g}$ phonon, respectively. Fig. 6(d) shows that there is a substantial decrease in the normalized $T_{1g}$-symmetry magnon intensity of CoCr$_2$O$_4$ with increasing field in both the Faraday ($k \parallel M \parallel H$) and Voigt ($k \perp M \parallel H$) geometries at $T = 10$ K and $T = 55$ K. Note that the field-dependent decrease we observe in the $T_{1g}$-symmetry magnon intensity—which is particularly dramatic in the Faraday geometry ($k \parallel M \parallel H$) —cannot be attributed to field-dependent changes in polarization or crystallographic orientation: the use of circularly polarized incident light in these experiments precludes field-dependent rotation of the incident polarization; and $T_{1g}$-symmetry modes appear in the depolarized scattering geometry independent of the crystallographic orientation of the sample.

**B. Discussion and Analysis**

The anomalously large decrease in the 16 cm$^{-1}$ $T_{1g}$-magnon Raman intensity with increasing field in the Faraday geometry ($k \parallel M \parallel H$) of CoCr$_2$O$_4$ (see Fig. 6) is quite different than the field-independent magnon Raman intensities observed in other spinel materials, such as Mn$_3$O$_4$ and MnV$_2$O$_4$.\textsuperscript{36} To clarify the anomalously strong field-dependence of the $T_{1g}$-symmetry magnon Raman intensity in CoCr$_2$O$_4$, note that the magnon Raman intensity in the Faraday geometry is expected to be dominated by the linear magnetic birefringence contribution to dielectric fluctuations, $\delta \epsilon = g(\delta l)^2$.\textsuperscript{52,55,56} Thus, the strong decrease in the $T_{1g}$-symmetry magnon Raman intensity in the Faraday geometry likely reflects a field-induced decrease in fluctuations of the antiferromagnetic vector, $\delta l$. A similar field-dependent decrease in the single-magnon inelastic light scattering response associated with fluctuations of the antiferromagnetic vector was also observed in the canted antiferromagnet EuTe.\textsuperscript{52}

Fig. 6(b), 6(d) shows that there is a similar, albeit less dramatic, field-dependent decrease in the $T_{1g}$-symmetry magnon Raman intensity measured in the Voigt ($k \perp M \parallel H$) geometry. This geometry is primarily sensitive to the Faraday ($\delta \epsilon = i f \delta m$) and isotropic exchange ($\delta \epsilon = a(\delta m)^2$) contributions to dielectric fluctuations, which are dominated by longitudinal fluctuations in the magnetization.\textsuperscript{52,55,56} Altogether, the suppression of the $T_{1g}$-symmetry magnon Raman scattering intensities in both Faraday and Voigt geometries is indicative of a field-induced suppression of both transverse and longitudinal magnetic fluctuations in CoCr$_2$O$_4$.

The field-dependent suppression of the $T_{1g}$-symmetry magnon Raman intensity in CoCr$_2$O$_4$ points to a specific microscopic mechanism for the magnetodielectric response observed in CoCr$_2$O$_4$.\textsuperscript{17,20,43} Lawes et al. have pointed out that the field-induced suppression of magnetic fluctuations can contribute to the magnetodielectric response of a material via the coupling of magnetic fluctuations to optical phonons.\textsuperscript{16} This spin-phonon coupling contributes to the magnetodielectric response of a material through field-induced changes to the net magnetization.\textsuperscript{15–17,58} A simple phenomenological description for how the magnetization of a magnetoelectric material influences the dielectric response of the material is obtained by considering the free energy, $F$, in a magnetoelectric material with a coupling between the magnetization $M$ and polarization $P$:\textsuperscript{15,17,58}

$$ F(M, P) = F_0 + aP^2 + bP^4 - PE + cM^2 + dM^4 - MH + eM^2P^2, $$

(2)

where $F_0$, $a$, $b$, $c$, $d$, and $e$ are temperature-dependent constants, and $M$, $P$, $E$, and $H$ are the magnitudes of the magnetization, polarization, applied electric field, and applied magnetic field, respectively. The dependence of the dielectric response on magnetization in a magnetoelectric material, $\epsilon(M)$, can be obtained from the second derivative of the free energy with respect to polarization $P$:\textsuperscript{15,17,58}

$$ [\epsilon(M)]^{-1} \sim (\partial^2 F / \partial P^2) = 2a + 12bP^2 + 2eM^2, $$

(3)

which, for a negligible macroscopic polarization $P$ in the material, can be written:\textsuperscript{15,17}

$$ \epsilon(M) = 1/[2a + 2eM^2]. $$

(4)

Thus, the dielectric response, $\epsilon = 4\pi \chi_E$, decreases with increasing squared magnetization, $M^2$ and decreasing magnetic fluctuations.\textsuperscript{16} The above results suggest that both the magnetic-field-dependent decrease in the intensity of the 16 cm$^{-1}$ $T_{1g}$-symmetry magnon (see Fig. 6) and the magnetodielectric response, $\Delta \epsilon(H)/\epsilon(0) = [\epsilon(H) - \epsilon(0)]/\epsilon(0)$, in CoCr$_2$O$_4$\textsuperscript{17,43} reflect magnetic-field-induced changes to magnetic fluctuations—particularly fluctuations associated with the antiferromagnetic vector—that are strongly coupled to phonons\textsuperscript{16} via the biquadratic contribution to the free energy, $M^2P^2$ (see Eq. (2)).

**V. PRESSURE DEPENDENCE OF THE $T_{1g}$-SYMMETRY MAGNON IN COCr$_2$O$_4$**

**A. Results**

As discussed above, the strong $T_{1g}$-symmetry magnon Raman intensity of CoCr$_2$O$_4$ is believed to reflect
strong magnetic fluctuations that are coupled to long-wavelength phonons, which should also be associated with significant magneto-optical responses (both linear Faraday and linear magnetic birefringence) in CoCr$_2$O$_4$. Our results show that the application of a magnetic field suppresses these fluctuations, leading to the substantial magnetodielectric response observed in CoCr$_2$O$_4$. An alternative approach to suppressing magnetic fluctuations is to use applied pressure or strain to increase the crystalline anisotropy of CoCr$_2$O$_4$. To investigate this possibility, magnetic-field-dependent measurements of the T$_{1g}$-symmetry magnon in CoCr$_2$O$_4$ were performed for different applied pressures.

Fig. 7 shows the field-dependence of the T$_{1g}$-symmetry magnon spectrum of CoCr$_2$O$_4$ in the Faraday ($\mathbf{k} \parallel \mathbf{M} \parallel \mathbf{H}$) geometry for different applied pressures at $T = 10$ K. Fig. 8(a) summarizes the field dependence of the T$_{1g}$-symmetry magnon energy at $T = 10$ K for different applied pressures, and Fig. 8(b) shows the amplitude of the T$_{1g}$-symmetry magnon Raman susceptibility (normalized by the amplitude of the 199 cm$^{-1}$ T$_{2g}$ phonon susceptibility) at $T = 10$ K for different applied pressures. The inset of Fig. 8(b) summarizes the pressure-dependence of the T$_{1g}$-symmetry magnon energy in CoCr$_2$O$_4$ for $H = 0$ T and $T = 10$ K.

B. Discussion and Analysis

The inset of Fig. 8(b) shows that the T$_{1g}$-symmetry magnon energy increases linearly with applied pressure at a rate of $d\omega/dP = 0.46$ cm$^{-1}$/kbar. This increase likely reflects a systematic increase in the anisotropy field, $H_A$, with increasing pressure, according to the relationship $\omega \sim (2H_A H_E)^{1/2}$. Additionally, the magnetic field dependence of the Raman spectrum of CoCr$_2$O$_4$ at different fixed pressures summarized in Fig. 8(a) shows that the field-dependent slope associated with the T$_{1g}$-symmetry magnon frequency, $d\omega/dH$, is insensitive to applied pressure up to roughly 21 kbar, indicating that the gyromagnetic ratio associated with Co$^{2+}$ is not strongly affected by these pressures in CoCr$_2$O$_4$.

On the other hand, Figs. 7 and 8 also show that $H = 0$ T$_{1g}$-symmetry magnon Raman intensity, Im $\chi(\omega)$, systematically decreases relative to the T$_{2g}$ phonon intensity, illustrating that increasing pressure suppresses the magnetic fluctuations and the magneto-optical response in CoCr$_2$O$_4$ by increasing the anisotropy field. Additionally, Fig. 8(b) shows that increasing pressure reduces the strong suppression of the T$_{1g}$-symmetry magnon intensity with increasing magnetic field in the Faraday geometry ($\mathbf{k} \parallel \mathbf{M} \parallel \mathbf{H}$), providing evidence that the magnetodielectric response of CoCr$_2$O$_4$ decreases with increasing pressure. Altogether, these results show that by tuning magnetic anisotropy and reducing magnetic fluctuations of the Co$^{2+}$ spins, pressure and epitaxial strain can be used as effective tuning parameters for controlling the magnetodielectric response of CoCr$_2$O$_4$.

VI. SUMMARY AND CONCLUSIONS

In this paper, we showed that the $q = 0$ T$_{1g}$-symmetry magnon in CoCr$_2$O$_4$ exhibits an anomalously large Raman scattering intensity, which reflects a large magneto-optical response that likely results from large magnetic fluctuations that couple strongly to the dielectric re-
The strong suppression of the T$_{1g}$-symmetry magnon Raman intensity in an applied field is consistent with the magnetodielectric response observed previously in this material, and suggests that the strong magnetodielectric response in CoCr$_2$O$_4$ results from the magnetic-field-induced suppression of magnetic fluctuations that are strongly coupled to phonons. Using pressure to increase the magnetic anisotropy in CoCr$_2$O$_4$, we found that we can suppress the magnetic field-dependence of the T$_{1g}$-symmetry magnon Raman intensity by suppressing magnetic fluctuations, demonstrating that pressure or epitaxial strain should be an effective means of controlling magnetodielectric behavior and the magneto-optical response in CoCr$_2$O$_4$. This Raman study also reveals conditions that are conducive for the substantial magneto-optical responses and magnetodielectric behaviors in materials, including the presence of strong spin-orbit coupling and weak magnetic anisotropy, both of which create favorable conditions for large magnetic fluctuations that strongly modulate the dielectric response.

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