Impact of the lattice on magnetic properties and possible spin nematicity in the S=1
triangular antiferromagnet NiGa$_2$S$_4$.

Michael E. Valentine,¹ Tomoya Higo,²,³ Yusuke Nambu,²,⁴ Dipanjan Chaudhuri,¹
Jiajia Wen,¹ Collin Broholm,¹,²,⁶ Satoru Nakatsuji,²,³,¹,⁷,⁸ and Natalia Drichko¹

¹Institute for Quantum Matter and Department of Physics and Astronomy,
Johns Hopkins University, Baltimore, MD 21218, USA
²Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan
³CREST, Japan Science and Technology Agency, Kawanachi, Saitama 332-0012, Japan
⁴Institute for Materials Research, Tohoku University, Sendai, Miyagi 980-8577, Japan
⁵NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA
⁶Department of Materials Science and Engineering, Whiting School,
Johns Hopkins University, Baltimore, MD 21218, USA
⁷Department of Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan
⁸Trans-scale Quantum Science Institute, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

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NiGa$_2$S$_4$ is a triangular lattice S=1 system with strong two-dimensionality of the lattice, actively
discussed as a candidate to host spin-nematic order brought about by strong quadrupole coupling.
Using Raman scattering spectroscopy we identify a phonon with E$_g$ symmetry which can modulate
magnetic exchange $J_1$ and produce quadrupole coupling. Additionally, our Raman scattering re-
results demonstrate a loss of local inversion symmetry on cooling, which we associate with sulfur
vacancies. This will lead to disordered Dzyaloshinskii-Moriya interactions, which can prevent long
range magnetic order. Using magnetic Raman scattering response we identify 160 K as a tempera-
ture of an upturn of magnetic correlations. The temperature below 160 K, but above 50 K where
antiferromagnetic magnetic start to increase, is a candidate for spin-nematic regime.

Magnetic frustration is an active area of research that
drives discoveries of new quantum phenomena [1, 2].
While much of this work is motivated by the search for a
quantum spin liquid, various novel types of spin order
have been predicted and discovered experimentally. Ex-
otic spin states or unsolved problems can be found even
for a simplest example of a frustrated system, a triangular
lattice. Nearest neighbor Hiesenberg antiferromagnetic
interactions in such a system with S=1/2 result in 120º
spin order. This order can be prevented by a presence of
magnetic interactions beyond nearest neighbor ones. For
example, in organic molecular Mott insulators, a pres-
ence of a ring exchange results in a spin liquid state [3].
In this work we address one example of a triangular lat-
tice system, where the absence of long range magnetic
order is not yet understood, despite much effort. This
system is NiGa$_2$S$_4$. It was actively discussed in a con-
text of nematic order, originating from large bi-quadratic magnetic exchange [4, 7].

In NiGa$_2$S$_4$ structure, an undistorted 2D triangular
lattice of Ni$^{2+}$ (S = 1) is formed in the ab plane from
edge-sharing Ni$_4$ octahedra [8] (Fig. 1c). Additional
layers of non-magnetic GaS$_4$ tetrahedra are positioned
between Ni layers along c axis. This results in a highly
two-dimensional structure, with negligibly small mag-
netic interactions between Ni planes.

Neutron scattering [8, 9] results have been explained
in terms of antiferromagnetic correlations with the wave
vector near (1/6,1/6,0), appearing on a triangular lattice
with a ferromagnetic nearest-neighbor superexchange $J_1$
= -0.4 meV, and an antiferromagnetic third nearest ex-
change $J_3 = 2.8$ meV [3] (see Fig. 1c). Values of exchange
interactions obtained by other methods and calculations
vary a lot [10], but agree on an importance of both ex-
changes. Both competing interactions and low dimen-
sionality of the system can lead to the observed suppres-
sion of long range magnetic order for this system where
$\Theta_W = -80$ K [8]. On lowering the temperature below
8 K the system undergoes a gradual spin freezing [11].

The absence of spin order, with spin dynamics slowing
down from about 50 K [9] has led to various theoretical
proposals of a spin-nematic state in NiGa$_2$S$_4$ [4,7]. Most
models suggest ferro-nematic order, where full rotational
symmetry of spin is broken, and it is confined to a certain
plane defined by a “director that characterizes the order
(Fig. 1c) [12]. Spin-nematic state is also an important
starting point in the theoretical explanation for the spin
freezing at 8 K, which occurs in NiGa$_2$S$_4$ in the presence
of only few per cent of sulfur vacancies [4, 13].

Spin-nematic order is difficult to confirm experiment-
ally. An important step is to identify an origin of a
large bi-quadratic exchange $K_q$ necessary to establish
spin-nematic order [4, 7]. As shown in Ref. [14, 15], $K_q$
can naturally arise from a second term of an expression
for magnetoelastic coupling $J = J_0 + \frac{\partial^2}{\partial \delta \delta} \Delta r_{ij} + \ldots$ and
elastic response of the lattice, when a phonon with a
displacement $\Delta r_{ij}$ modulates magnetic exchange or su-
perexchange $J$. A bi-quadratic term $K_q$ which could
arise from a phonon modulating $J_3$ can be enhanced in
NiGa$_2$S$_4$ due to the unique near-90º Ni-S-Ni bond angle,
as proposed in Ref. [4]. Here we use Raman scatter-
ing spectroscopy and Density Functional Theory (DFT)
FIG. 1. (a) Crystal structure of NiGa$_2$S$_4$. (b) Schematic structure of triangular lattice of Ni with $J_1$ and $J_3$ super-exchanges through S2 atoms marked. (c) Schematic view of the incommensurate short range order from Ref. [8] (d) Schematic view of spin-nematic order on triangular lattice with director $d$ perpendicular to the (ab) plane. Grey circles depict $S_z$=0 states.

phonons calculations to identify such a phonon. In addition, Raman scattering has been theoretically suggested to be a probe of spin quadrupole excitations [16]. To identify magnetic excitations in Raman spectra we provide a comparison to inelastic neutron scattering data.

Besides these effects directly related to the magnetism in NiGa$_2$S$_4$, we present evidence for previously undetected local inversion symmetry breaking. The effect develops independently from magneto-elastic (ME) coupling, and the amplitude of the corresponding signal increases on cooling. We associate this lattice deformation with sulfur vacancies [17] that by symmetry enable random Dzyaloshinskii-Moriya (DM) interactions.

The magnetic susceptibility $\chi(T)$ of NiGa$_2$S$_4$ increases on cooling, and shows flattening associated with spin freezing at temperatures below 8 K [18]. Here we focus on the uniaxial anisotropy of the magnetic susceptibility in magnetic field from 0.01 T to 5 T at temperatures between 2 K and 300 K, measured using a commercial SQUID magnetometer (MPMS, Quantum Design). Magnetic field $H$ was directed parallel to the crystallographic $c$ axis ($\chi_c$) and parallel to the (ab) plane ($\chi_{ab}$). In the temperature range from 200 K to 50 K, no considerable anisotropy $\chi_{ab}/\chi_c$ is observed. Below 50 K, for all measured magnetic fields anisotropy of susceptibility $\chi_{ab}/\chi_c$ increases on cooling, reaching a maximum at spin freezing temperature around 8 K (Fig. 2a).

This anisotropy indicates a development of in-(ab) plane magnetic correlations. When the material enters a frozen spin state, $\chi_{ab}/\chi_c$ decreases again. The maximum of the anisotropy at low temperatures is suppressed by magnetic fields above 0.025 T; a weaker magnetic anisotropy with $\chi_{ab}/\chi_c(12 \text{ K}) = 1.2$ at 8 K is preserved up to the highest measured field of 5 T (Fig. 2b).

Fig. 3 shows the Raman scattering spectra of NiGa$_2$S$_4$ for temperatures between 300 K and 8 K. Raman scattering was excited by 514.5 nm (2.4 eV) line of Coherent Ar$^+$ laser, and measured using T64000 Horiba Jobin-Yvon spectrometer. Spectra were measured from the (ab) plane of the crystals, in (x, x) and (x, y) geometries ($x \perp y$), which correspond to the A$_{1g}$ and E$_g$ scattering channels for the D$_{3d}$ point group associated with trigonal $P\bar{3}m1$ space group of NiGa$_2$S$_4$. Raman spectra of NiGa$_2$S$_4$ comprise of a superposition of forbidden modes and magnetic excitations, in addition to Raman-active phonons. Five of six ($\Gamma_R = 3A_{1g} + 3E_g$) Raman-active phonons appear in the spectra as sharp intense peaks (see Supplemental Information (SI)). Here we focus on the two phonons at 206 and 450 cm$^{-1}$ that involve movement of sulfur atoms S2 that form NiS$_6$ octahedra (see Fig. 3). These are of a special interest, since S2 mediate all magnetic interactions in NiGa$_2$S$_4$ (see Fig. 1b). The sulfur S2 motion associated with these two phonons modulates the nearest neighbor exchange interactions $J_1$ ($\delta J_1/\delta r$, where $r$ is a change of S2 coordinate) in two different ways (see Fig. 3). The A$_{1g}$ phonon at 450 cm$^{-1}$ corresponds to the out-of-plane movement of S2 atoms, which modulates the sign of $J_1$, but preserves the symmetry of triangular lattice. The E$_g$ phonon at 206 cm$^{-1}$ on the other hand maintains the sign of $J_1$, while dynamically breaking $C_3$ symmetry of the Ni-S2-Ni bonds.

Experimentally, we find an essential difference in the magneto-elastic coupling for these two phonons, demonstrated by the temperature dependence of their line widths (Fig. 3c). In the absence of magneto-elastic coupling, a phonon line width is determined by phonon-phonon scattering [18]. It follows the general formula $\Gamma(T, \omega) = \Gamma_0 + A(2\nu_B(\omega/2) + 1)$, where $\Gamma_0$ is a temperature independent term defined by disorder. This formula describes well the temperature dependence of the width of the A$_{1g}$ mode at 450 cm$^{-1}$ (Fig. 3c, black squares are experimental points, a solid line is the fitting curve). In contrast, the width of the E$_g$ phonon at 206 cm$^{-1}$ starts to deviate from the conventional behavior at about 150 K, and decreases below 50 K. Moreover, the E$_g$ phonon at 206 cm$^{-1}$ shows a characteristic asymmetric Fano line shape, which is typically a result of an interaction between a single level of a phonon mode and an underlying continuum. The line shape is described...
A positive coupling parameter \( q \) and the creation of pairs of magnons with momenta between neighboring sites of different sublattices, leads to the phonon frequency (see more details in SI).

Atomic displacements for \( E_{c,0} \) indicate that the continuum of excitations lies above 100 cm\(^{-1}\)(12 meV). According to Raman spectra, it extends to frequencies above 500 cm\(^{-1}\)(60 meV).

Upon heating, the low-frequency continuum starts to broaden, while the maximum does not change its position considerably. We estimate the scattering rate by a Lorentzian fit of the low-frequency maximum as indicated in Fig. 3a as indicated by the hatched area at 10 K. Scattering rate \( \Gamma(T) \) shows linear increase with temperature up to 120 K (red curve in Fig. 4b). This behaviour, \( \Gamma(T) = (\xi_T)^{-2}\Gamma(0) \), where \( \xi \) is a correlation length is expected for critical fluctuations close to an AF transition for a simple mean field dependence of correlation length on temperature: \( \xi \sim \xi_0(1 + T/T_c)^{\alpha} \) [23-26]. Above 120 K \( \Gamma(T) \) starts to grow faster than linear dependence, and at temperatures above 160 K (Fig. 4b, red curve) the shape of the continuum changes. It becomes incoherent, with a much broader maximum at somewhat higher frequencies around 200 cm\(^{-1}\) (see SI for a more detailed temperature dependence). This change of the shape of the Raman continuum from "critical" fluctuations observed below approximately 160 K into a "diffusive" background typical for any paramagnet at higher temperatures shows a change of the nature of spin-spin correlations in NiGa\(_2\)S\(_4\).

The temperature of 160 K up to which Raman scattering can trace AF fluctuations is considerably higher than 50 K, up to which NS could detect short range AF correlations in NiGa\(_2\)S\(_4\) [9, 27]. Interestingly, anisotropy of the magnetic susceptibility \( \chi_{ab}/\chi_c \) (see Fig. 4 black points) starts to increase for \( T < 50 \) K, when AF spin correlations start to develop.

Calculations for the \( J_1-J_3-K_q \) model [4] suggest a lower-temperature regime where AF spin correlations are present, while at higher temperatures spin-nematic magnon shift. In combination these data indicate that two-magnon excitations produce a broad maximum around 100 cm\(^{-1}\)(12 meV). According to Raman spectra, it extends to frequencies above 500 cm\(^{-1}\)(60 meV).
interactions prevail. Theoretical calculations for spin-nematic order of a S=1 system on a square lattice with bi-quadratic interactions $K_g$ [16] suggested that Raman spectra of a quadrupole ordered state would consist of a band at about $5K_g$, and an order of magnitude weaker excitations bands in the region of $10K_g - 12K_g$, twice the energy of the low-frequency continuum. Spectra at temperatures between 50 and 160 K (Fig. 4a) demonstrate a very broad continuum extending all the way to 60 meV. At 10 K we can separate a low-frequency part of the continuum with a maximum at 12 meV, and a much lower intensity continuum at frequency around 50 meV. The asymmetric shape of the $E_g$ phonon at 206 cm$^{-1}$, as well as slight asymmetry of $A_g$ phonon at 450 cm$^{-1}$ suggest that they couple to the continuum states in the range of 25 to 50 meV. While these higher-frequency excitations may be the candidate for quadrupole excitations, suggested in Ref. [16], measurements with a higher excitation beam frequency is needed for conclusive results.

Unexpectedly, and seemingly unrelated to the magnetic properties NiGa$_2$S$_4$, our Raman study finds changes of the lattice symmetry on cooling. In addition to the narrow bands of Raman-active phonons, and the continuum of magnetic excitations, we observe broad features which do not show distinct polarization dependence (Fig. 5a, upper panel). Their intensity increases linearly on cooling, as demonstrated in Fig. 5a for the features at 270 and 296 cm$^{-1}$. Comparison to $\epsilon_2$ spectra obtained from our IR reflectance measurements at T=4 K-300 K (see SI) shows, that these bands correspond to infrared-active phonons, as easily recognized for the most intense lines of $E_u$ phonons at 270 and 296 cm$^{-1}$ marked on the Fig. 5a, lower panel, with dashed lines. $D_{3d}$ symmetry of the unit cell of NiGa$_2$S$_4$ restricts phonon modes to being either Raman or IR active [28]. The appearance of $E_u$ and $A_{2u}$ IR modes in the Raman spectrum is an indication of a loss of inversion symmetry. The absence of anomalous broadening or splitting of all $E_u$ and $E_g$ phonons (for detail see SI) indicates that in-plane $C_3$ symmetry is unperturbed. To the best of our knowledge, no structural transition or crossover in NiGa$_2$S$_4$ was previously reported. However, sulfur vacancies, which are present in NiGa$_2$S$_4$ [13] can break local symmetry. Local point group symmetries consistent with our observations are $C_3$ and $C_{3s}$. This means, that local deformation of the lattice around a vacancy has a dominant component parallel to the c-axis, while preserving isotropic triangular lattice of Ni atoms in the (ab) plane.

The increase of the intensity of the IR modes in the Raman spectrum upon cooling suggests that the amplitude of these local deformations of the lattice increases, possibly due to anisotropic thermal contraction. At low temperatures the intensity of the IR lines becomes comparable to that of the Raman-active modes. For local symmetry breaking confined to unit cells with a vacancy, the estimated less than 2% of sulfur vacancies [13] cannot produce such a large effect. This suggests that the symmetry breaking impact of each vacancy goes beyond a single unit cell, but does not lead to a global long-range order.

To summarize, we observe two different lattice-related effects in NiGa$_2$S$_4$. One is magneto-elastic coupling, the other is local loss of inversion symmetry. Both can produce considerable effects on the magnetic properties of NiGa$_2$S$_4$.

The $E_g$ phonon at 206 cm$^{-1}$ shows evidence of magneto-elastic coupling. It can modulate $J_1$, and lead to a bi-quadratic exchange $K_g$. DFT calculations calculation are needed to estimate the size of the effect.

The local loss of inversion symmetry due to vacancies can be an additional factor preventing magnetic ordering. According to Ref. [13], S1 sites, which are not directly involved in superexchange, are more susceptible to sulfur loss. The distortion of the lattice around a vacancy can randomly change chemical bonds that determine $J_1$ and $J_3$. Additionally, the loss of inversion symmetry allows for Dzyaloshinskii-Moriya interactions, which were not previously discussed for NiGa$_2$S$_4$, but which can also affect magnetic ordering. Besides, we observed a reduction of in-plane anisotropy $\chi_{ab}/\chi_c$ below the spin freezing temperature. Deformation of the lattice along the c-axis could lie behind this effect.

In agreement with heat capacity, Raman scattering distinguishes three distinct temperature regimes for NiGa$_2$S$_4$:

In the temperature range between 300 and 160 K, no magneto-elastic coupling or antiferromagnetic fluctuations related to low-temperature magnetic state are observed in the Raman scattering. Between approximately 160 and 50 K, the magnetic susceptibility is isotropic, but magnetic Raman scattering identifies the development of local spin correlations. Magneto-elastic coupling is observed for $E_g$ phonon. This points on a spin-nematic
regime, but with director that is not pinned to the c-axis.

Below 50 K, short range dynamic spin correlations are identified by neutron scattering [9], with correlation length that increases on cooling, in agreement with further narrowing of the Raman low-frequency magnetic continuum. In this regime the easy-plane anisotropy of the magnetic susceptibility increases as well. Interestingly, magneto-elastic coupling for the $E_g$ phonon which modulates $J_1$ also increases in this regime. Our measurements of the field dependence of magnetic anisotropy show that application of only 0.025 T is enough to suppress the easy plane anisotropy, while according to NS experiments [9] a much higher field of 5 T is needed to suppress interplane AF correlations.

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* Corresponding author: drichko@jhu.edu

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SUPPLEMENTAL MATERIAL

Crystal growth and preparation for measurements

NiGa$_2$S$_4$ single crystals were grown using the method outlined in Ref. [30]. The resulting crystals are thin plates with the most developed surface parallel to $ab$ plane measuring up to 3 mm by 3 mm and thickness 10 $\mu$m.

In preparation for measurements, the samples were cleaved to ensure optimum concentration of sulfur in the probed sample. Raman scattering showed reproducible data for spectra measured from cleaved surfaces of different crystals. Magnetic susceptibility measurements showed the transition into the spin frozen state at 8 K, which corresponds to the best quality crystals with less than 4% sulfur vacancies [13].

Neutron scattering measurements

The neutron scattering experiment was carried out on the MACS instrument at the NIST Center for Neutron Research. 19 single crystals of NiGa$_2$S$_4$ with total mass $\sim$1 g were co-aligned in the ($H K 0$) plane for the measurement. A final neutron energy of $E_f = 3.6$ meV was used for measurements with energy transfer $E \leq 4.5$ meV, while $E_f = 5$ meV was employed for measurement with $E \geq 4.5$ meV. All measurements were normalized to the monitor counts that corresponds to 1 minute counting with incident neutron energy $E_i = 3.6$ meV. An aluminum sample with similar mass to the sample holder as well as the empty cryostat were measured separately at all experimental settings for background subtraction. The one-magnon density of states $\rho_1(E)$ is calculated by integrating the neutron scattering intensities measured at $T = 2$ K over a common region in the second Brillouin zone, which is accessible for all energy transfer. Under the assumption that the crystal momentum remains a good quantum number, the two-magnon density of states probed by Raman scattering $\rho_2(E)$ is related to the one-magnon density of states by $\rho_2(E) \sim \rho_1(E/2)$, which is found to agree well with the Raman measurements.

Raman scattering spectroscopy

The crystals of NiGa$_2$S$_4$ are shaped as thin plates, thus spectra in $(c,c)$ polarization ($(z,z)$ scattering channel) were measured only at room temperature using a micro-Raman setup, while spectra in the $(a,b)$ plane were measured down to 4 K using a combination of macro and micro-Raman setups. Spectra in the $(a,b)$ plane were measured from freshly cleaved surfaces.

The main Raman scattering data were obtained using a macro-Raman setup based on a Jobin-Yvon T64000 Raman spectrometer in a single monochromator configuration in a pseudo-Brewster’s angle scattering geometry. Measurements at temperatures from 300 K to 4 K in the frequency range between 100 cm$^{-1}$ and 600 cm$^{-1}$ were performed using a 514.5 nm line of an Ar$^+$-Kr$^+$ Coherent laser for excitation. Laser power did not exceeding 4 mW for a laser probe of $\sim 50 \times 100 \mu$m to avoid overheating of the sample. The sample was attached to the cold finger of Janis ST500 cryostat. Additional room temperature measurements of NiGa$_2$S$_4$ crystals in $(c,c)$ polarization in the 100 cm$^{-1}$ to 600 cm$^{-1}$ spectral range were obtained using the Jobin-Yvon T64000 Raman spectrometer equipped with Olympus microscope with the spot diameter of 2 $\mu$m. Phonon spectra in the frequency range from 10 cm$^{-1}$ to 600 cm$^{-1}$ with resolution 5 cm$^{-1}$ were obtained using a Jobin-Yvon U1000 spectrometer equipped with a photomultiplier detector, in a pseudo-Brewster’s angle scattering geometry. 514.5 nm line of an Ar$^+$ laser was used as excitation light with a beam size on the sample of $\sim 50 \mu$m $\times 100 \mu$m. Low temperature measurements were performed using a custom built Janis cold finger cryostat.

All presented spectra are normalized by a first-order Bose-Einstein thermal factor $n(\omega) + 1$.

The NiGa$_2$S$_4$ structure is described by the trigonal $P\bar{3}m1$ space group, which corresponds to the $D_{3d}$ point group symmetry with the following Raman tensors:

$$A_{1g} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$$

$$E_g = \begin{pmatrix} c & 0 & 0 \\ 0 & c & d \\ 0 & d & 0 \end{pmatrix}, \begin{pmatrix} -c & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & -d \end{pmatrix}.$$

Based on these Raman tensors, the intensities for the different measured polarizations of $e_i$ electrical vector of the excitation light and $e_s$ of the Raman scattered light can be decomposed as

$$I_{xx} = |a|^2 + |c|^2, I_{xy} = |c|^2, I_{zz} = |b|^2$$

where $x \perp y$ denote $e_i$ and $e_s$ lying in the $(ab)$ plane, and $z$-polarized light is parallel to the out of plane $c$ axis. Discrepancies between the theoretical and the observed polarization dependence can be attributed to the depolarization that occurs at the crystal surface in all non-backscattering geometries.

Raman data and data analysis:

DFT calculations The frequencies of the phonons at the $\Gamma$ point of the BZ and the respective atomic displacements were calculated using density functional theory (DFT) calculations with Quantum Espresso software with the PHonon package [31] based on the average structure determined by x-ray diffraction measurements [13].
A generalized gradient approximation was used for the exchange-correlation in the energy functional.

Assignment of phonons in experimental spectra The observed phonon frequency assignment is based on our DFT calculations. Of six Raman-active ($A_{1g}$ and $E_g$) NiGa$_2$S$_4$ phonons (Table I) we observe five (Fig. 6). Another $E_g$ mode expected at 285 cm$^{-1}$ is observed as a very weak band in $(x,y)$ spectra. Likely it is more intense for $\chi''_{zz}$, $\chi''_{yy}$ ($d$ in the above Raman tensors), for which no measurements were performed. Frequencies of all the phonons observed in IR and Raman spectra and their assignment based on our DFT calculations are listed in Table I. Calculated frequencies show a good agreement with the experiments except for the highest frequency $A_{1g}$ phonon, which is observed at frequencies significantly higher than the calculation suggests.

Phonon Raman spectra in the frequency range between 10 and 200 cm$^{-1}$ are presented in Fig. 8a. They show two lowest lying phonons, $E_g$ at about 42 cm$^{-1}$, and $A_{1g}$ at about 120 cm$^{-1}$. Note that $E_g$ phonon is not broadened on cooling, in contrast to the $E_g$ at 206 cm$^{-1}$.

**Table I: Wyckoff positions and $\Gamma$-point representations for NiGa$_2$S$_4$, including $A_{2u} + E_u$ acoustic modes. $A_{1g}$ and $E_g$ phonons are Raman active.**

| Element | Wyckoff position | $\Gamma$ representation |
|---------|------------------|--------------------------|
| Ni      | 1b               | $A_{2u} + E_u$           |
| Ga      | 2d               | $A_{1g} + E_g + A_{2u} + E_u$ |
| S1      | 2d               | $A_{1g} + E_g + A_{2u} + E_u$ |
| S2      | 2d               | $A_{1g} + E_g + A_{2u} + E_u$ |

**FIG. 6. Raman phonon spectra of NiGa$_2$S$_4$ at room temperature measured in 10-600 cm$^{-1}$ spectral range. (x, x) and (x, y) are polarizations randomly oriented within the (ab) plane. (z, z) polarization measured using micro-Raman setup. Five Raman-active phonons are marked with arrows. Broad low-intensity features correspond to Raman-inactive vibrations, activated due to a local loss of inversion center.**

**FIG. 7. (a) Fano line shape of the $E_g$ phonon (206 cm$^{-1}$) at 250 K and 8 K. Black dotted lines show fitting curves.**

**Magneto-elastic coupling** Coupling of the $E_g$ phonon at 206 cm$^{-1}$ to a continuum of excitations is described by the Fano formula $F(\omega, \omega_F, \Gamma_F, q) = \frac{1}{\sqrt{\Gamma_F^2 - (\omega - \omega_F)^2}}$. We show in the main part of the text, that upon cooling, the width $\Gamma_F$ of the phonon obtained by least squares fitting of the spectrum increases. The temperature dependence of the width follows the growth of intensity of the continuum of magnetic excitations. In this formula, $q$ is an empirical coupling parameter, the value of which describes the strength of coupling, that depends on the spectral position of the continuum relative to the phonon $[20]$. The positive value of $q$ suggests that the continuum with which the $E_g$ phonon is interacting lies at frequencies above that of the phonon. The parameter $q$ has a very weak temperature dependence (Fig. 7 b), which indicates that continuum stays at constant frequencies in the whole measured temperature range.

**FIG. 8. (a) Raman phonon spectra of NiGa$_2$S$_4$ in the spectral range between 10 cm$^{-1}$ and 200 cm$^{-1}$ taken at 10 K, 25 K, and 90 K. Note the absence of broadening for the $E_g$ phonon at 42 cm$^{-1}$.**

**Raman-forbidden phonons subtraction** To analyse the continuum of magnetic excitations detected in Raman scattering spectra, we subtracted a contribution of the spectra related to Raman-forbidden phonons...
phonons ($\chi''_{\text{phonon}}(\omega)$), which appear in the spectra due to local symmetry breaking, from the total experimentally measured Raman scattering $\chi''(\omega)$. As clearly observed in Fig. 4a, upper panel, this contribution is isotropic, in contrast to the narrow bands of Raman-active phonons. This isotropic contribution $\chi''_{\text{phonon}}(\omega)$ was fitted with a sum of Lorenzian spectral shape, and subtracted from the spectra at each temperature: $\chi''(\omega)_{\text{magnetic}} = \chi''(\omega) - k(T)\chi''(\omega)_{\text{phonon}}$.

In addition to the data in Fig. 4a, in Fig. 8a we present a temperature dependence of the magnetic Raman continuum measured in $(x,y)$ configuration, obtained by this subtraction.

**Low temperature IR spectra**

**IR spectroscopy** A Bruker Fourier transform infrared (FTIR) spectrometer with a bolometer detector was used to obtain the reflection infrared spectrum across an energy range from 150 cm$^{-1}$ to 600 cm$^{-1}$ with a resolution of 2 cm$^{-1}$. Spectra were measured with polarization of light $E \parallel (ab)$, where only modes with $E_u$ symmetry are observed. The absolute reflectance values were obtained by referencing the sample spectra to that of a sample with a gold film evaporated on its surface. Absorbance spectra were obtained from reflectance using Kramers-Kronig transformation. For measurements from 4 K to 300 K a cold finger cryostat Janis ST300 was used. The results are in general agreement with infrared measurements on powder NiGa$_2$S$_4$ samples [32].

![IR spectra](image)

**FIG. 9.** Temperature dependence of reflectivity spectra of NiGa$_2$S$_4$ with $E \parallel (ab)$

**Magnetic susceptibility**

The temperature dependence of the susceptibility $\chi(T) = M(T)/H$ at $H = 0.01$ and 5 T for the in plane ($\chi_{ab}$) and out-of-plane ($\chi_c$) direction is presented in Fig. 10 (a) and (b), respectively. Hysteresis between the field-cooled (FC) and zero-field-cooled (ZFC) data under 0.01 T is seen below a freezing temperature $T_{SF} = 7$ K. The Weiss temperature $\Theta_W = 83(1)$ K and the effective moments $p_{\text{eff}} = 2.81 \mu_B$/Ni are estimated by the Curie-Weiss law, $\Theta_W = C/(T\Theta_W)$ for temperatures 150 K $\leq T \leq 350$ K under 5T.

![Magnetic susceptibility](image)

**FIG. 10.** Temperature dependence of magnetic susceptibility of NiGa$_2$S$_4$ for the fields applied in the $(ab)$ plane and along the $c$-axis (right panel) at 0.01 and 5 T.
| Sym (pol) | Observed Raman bands | Observed IR | DFT calculations |
|----------|----------------------|-------------|-----------------|
|          | $\omega$ | $\gamma$ | Observed Pol. | $\omega$ | Ni | Ga | S1 | S2 |
| $A_{2u}(z)$ | 9 | 0.38 | 0.38 | 0.38 | 0.38 |
| $E_u(x)(y)$ | 18 | 0.38 | 0.38 | 0.38 | 0.38 |
| $E_{g}(xy)$ | 42 | 5 | $xx, xy, RR$ | 40 | 0.00 | 0.50 | 0.49 | 0.10 |
| $E_{u}(x)(y)$ | 62 | 0.54 | 0.30 | 0.28 | 0.44 |
| $A_{1g}(xx)$ | 118 | 0.00 | 0.44 | 0.50 | 0.24 |
| $A_{2u}(z)$ | 123 | 0.86 | 0.19 | 0.30 | 0.07 |
| $E_{g}(xy)$ | 198 | 0.00 | 0.06 | 0.00 | 0.70 |
| none | 233 | $xx$ |
| $E_{u}(x)(y)$ | 261 | 0.54 | 0.11 | 0.16 | 0.56 |
| $A_{2u}(z)$ | 284 | 0.12 | 0.08 | 0.52 | 0.46 |
| $E_{g}(xy)$ | 284 | 0.14 | 0.27 | 0.62 | 0.17 |
| $E_u$ | 284 | 0.14 | 0.27 | 0.62 | 0.17 |
| $A_{1g}$ | 316 | 0.00 | 0.21 | 0.57 | 0.34 |
| none | 335 |
| $A_{2u}$ | 354 | 0.03 | 0.37 | 0.33 | 0.50 |
| $A_{1g}$ | 408 | 0.00 | 0.25 | 0.18 | 0.63 |

TABLE II: Measured frequencies $\omega$ and widths $\gamma$ for the Raman and IR active modes and the polarizations in which they appear. The italic font is used for those bands, which appear in violation of the selection rules. The bands marked with * appears in [32]. Experimental frequencies are compared with those determined from calculations, and the relative displacements of each of the unique atomic positions is shown.