nature portfolio

Peer Review File

Unconventional insulator-to-metal phase transition in Mn3Si2Te6

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The authors report the optical reflectivity in $Mn_3Si_2Te_6$, which exhibits colossal angular magnetoresistance (CAMR) and a possible chiral orbital state. This system is particularly interesting as its CAMR is current-sensitive. The main findings of the present work are (1) the field-induced metallic state, which is responsible for the CAMR, is a bad metal without coherent carriers, and (2) the field-evolution of optical conductivity is well-described by a percolation model, implying electronic inhomogeneity. The system under study is of general interest to the community, and the present findings link $Mn_3Si_2Te_6$ to other inhomogeneous strongly correlated systems, which open the door for further studies using techniques developed for correlated systems over the decades. However, as there are competing theories for the unusual properties of $Mn_3Si_2Te_6$, it is important to clarify how the percolation model compares to other models of $Mn_3Si_2Te_6$, and ideally propose experimental tests to distinguish differing theories. I think this work could be suitable for publication in Nature Communications, if the authors can satisfactorily address the following issues:

(1) the electronic inhomogeneity implied in this work differs dramatically from the theories of CAMR in Refs. 21 and 17. The authors should highlight which features in the experimental data cannot be captured by previous models, clarify what kinds of field-evolution for the optical conductivity are expected in those models, and thus motivating the percolation model. The authors may also discuss further tests (maybe STM?) to distinguish different scenarios.

(2) Does the present model account for the strong angular dependence of the CAMR in Ref, 21, as well as the current-sensitive resistivity and time-dependent switching in Ref. 17? These are obviously challenging questions, and it should be sufficient to have qualitative arguments for how these behaviors may emerge in the present model.

(3) The experimental and calculated phonon intensities in Fig. 1b do not seem to match too well, why is this?

(4) The small spin-phonon coupling inferred from Fig. 2 are for q=0 phonons, is it possible to have a large spin-phonon coupling at a non-zero q that play a role in the CMR?

(5) Why is H0 frequency-dependent, is such a behavior seen in other CMR materials with electronic inhomogeneity?

Minor issues:

Several terms should be explained: ‘gap sequence’, line 91; ‘strong electronic features’, line 92; ’oscillator strength’ (what oscillator?), line 133; ’a new bound state’ (what bound state?), line 188.

S2 on line 160 is stated to be ‘measured values of …’, is it measured or a fit parameter? The ‘full field’ seems to be above the experimentally accessible limit.

Reviewer #2 (Remarks to the Author):

The team investigates the magneto-optical properties of Mn3Si2Te6, a nodal-line semiconductor, which has garnered much research attention in the recent past, owing to the occurrence of unusual CMR. This work attempts to shed additional light on such an unusual CMR effect by performing infrared spectroscopic measurements as a function of temperature and magnetic fields. The main discovery is the field-driven insulator-to-metal transition, which leads to a weakly metallic state

with localized carriers. The percolation model provided evidence for electronic inhomogeneity and phase separation.

These results are quite encouraging in the growing field of van der Waals magnetic materials and their emerging properties. The optical (reflectance) properties of this compound as a function of temperature and magnetic field have not been reported. I strongly believe that this work is original.

While this manuscript sounds quite rich in interpretation and analysis, its quality can be further improved by addressing the following comments.

1. From my perspective, it is quite useful to independently support the evidence for the presence of inhomogeneities and phase separation.

2. It is important to provide the materials characterization details such as XRD, XPS, etc to gain confidence in the quality of the crystals used for the measurements reported here.

3. It would be beneficial for the community to provide basic magnetic characterization to show the ferrimagnetic phase transition temperature.

4. This compound is known to show competing magnetic phases due to inequivalent Mn sites. One wonders if this is considered in the data analysis and interpretation.

5. Compounds like this tend to form a layer of TeO_2 on its surface. Have the authors considered the contribution coming from this layer while analyzing the data?

Reviewer #3 (Remarks to the Author):

$Mn_{33}Si_{22}Te_{66}$ is a compound that has attracted significant attention within the scientific community due to its unusual properties. The authors have made a substantial contribution towards understanding the insulator-to-metal transitions in this material. However, before recommending publication, the authors should address a few issues:

1. Appropriate error bars should be added in the main text and supplementary data, for example, in Figure 2 and Figure 4.

2. An anharmonicity model was used in Figure 2 for the analysis of the phonon energy temperature dependence. Why did the authors not consider lattice thermal expansion effects?

3. Can you comment on the 150 cm−1 phonon evolution around 150 K? Did you observe something similar as reported in Phys. Rev. B 107, 054309?

Response to Reviewer 1:

Referee 1 writes: *The authors report the optical reflectivity in $Mn_3Si_2Te_6$, which exhibits colossal angular magnetoresistance (CAMR) and a possible chiral orbital state. This system is particularly interesting as its CAMR is current-sensitive. The main findings of the present work are (1) the field-induced metallic state, which is responsible for the CAMR, is a bad metal without coherent carriers, and (2) the field-evolution of optical conductivity is well-described by a percolation model, implying electronic inhomogeneity. The system under study is of general interest to the community, and the present findings link $Mn_3Si_2Te_6$ to other inhomogeneous strongly correlated systems, which open the door for further studies using techniques developed for correlated systems over the decades. However, as there are competing theories for the unusual properties of $Mn_3Si_2Te_6$, it is important to clarify how the percolation model compares to other models of $Mn_3Si_2Te_6$, and ideally propose experimental tests to distinguish differing theories. I think this work could be suitable for publication in Nature Communications, if the authors can satisfactorily address the following issues:*

Our reply: Yes, nicely summarized! Thank you so much for your interest.

Referee 1 writes: *(1) the electronic inhomogeneity implied in this work differs dramatically from the theories of CAMR in Refs. 21 and 17. The authors should highlight which features in the experimental data cannot be captured by previous models, clarify what kinds of field-evolution for the optical conductivity are expected in those models, and thus motivating the percolation model. The authors may also discuss further tests (maybe STM?) to distinguish different scenarios.*

Our reply: Yes, both References 21 and 17 outline models for traditional insulator-to-metal transitions and CMR in combination with spin rotations and orbital loop currents. The surprise in our work is that we do not see a Drude metal at high magnetic fields. Instead, we find localized excitations which are not directly captured by models that propose CMR based upon spin rotations and topological band degeneracies as well as orbital currents. We added a simulation of this effect in Supplementary Note 6. The field dependence of carriers with different frequencies is also not included in prior models. The challenge going forward is to combine (i) transport which indicates almost 100% of CMR effects near 3 or 4 T, (ii) magnetic measurements supporting spin rotation and a gradual onset of the high field state, and (iii) localization physics from our infrared work that points toward a percolation model and electronic inhomegenity as well as a frequency-dependent response of the localized carriers. Likely mechanistic candidates include spin rotation models, spin-polaron models, orbital loop current models, and perhaps even Slater physics. We added a few sentences on the latter in the main text since the possibility of a Slater peak in the optical conductivity is an additional scenario that merits consideration.

We agree that real space measurements like STM, spatially-resolved ARPES, and near field infrared imaging may be important to unraveling these questions. Neutron-scattering can also help reveal whether there is any magnetic character to the localized excitations as expected for a Slater peak. We modified the following sentence in the main text to better

indicate that the jury is still out on these questions: "More work is obviously needed to clarify the matter, especially real space spectroscopies to reveal electronic inhomogeneities and neutron scattering to determine whether the localized excitation has a magnetic origin."

Referee 1 writes: *(2) Does the present model account for the strong angular dependence of the CAMR in Ref. 21, as well as the current-sensitive resistivity and time-dependent switching in Ref. 17? These are obviously challenging questions, and it should be sufficient to have qualitative arguments for how these behaviors may emerge in the present model.*

Our reply: Literature consistently reveals that CMR in $Mn_3Si_2Te_6$ is strong for $H \parallel c$ and significantly less for $H \perp c$. We therefore focused all of our magnet time on measurements in the most promising configuration. This strategy allowed us to measure three different samples in the $H \parallel c$ configuration. Since we did not measure with H along the "hard" axes, we can not weigh in on the angular dependence of the CMR.

On the other hand, we can compare our results with prior work. Some of what we find is consistent with previously proposed mechanisms. For instance, the gradual rise of the magnetization agrees with the gradual development of the localized excitation in the infrared, and the presence of a localized excitation may be consistent with orbital loop currents in the *ab* plane since carriers pinned at 300 cm^{-1} should have loops on the order of microns. The Slater mechanism, which has not been previously discussed, may play a role as well, so there is clearly still much to learn.

Referee 1 writes: *(3) The experimental and calculated phonon intensities in Fig. 1b do not seem to match too well, why is this?*

Our reply: Most of our calculated and measured phonon frequencies match within 5%, which is typical of most modern lattice dynamics calculations [Table S1, Supplementary Fig. 3a]. This level of agreement is more than enough to unambiguously assign all of the vibrational modes. That said, we also checked the U-dependence of the phonon features to confirm that our calculations are robust [Supplementary Fig. 3b)]. Theoretical intensities are of course always less reliable due to the difficulty in calculating the matrix element as opposed to the energy of the phonon mode. But in this case, they are pretty close.

Referee 1 writes: *(4) The small spin-phonon coupling inferred from Fig. 2 are for q=0 phonons, is it possible to have a large spin-phonon coupling at a non-zero q that play a role in the CMR?*

Our reply: Yes, absolutely. Our finding is that the $q = 0$ infrared-active phonons have small spin-phonon coupling. Certainly the $q = 0$ magneto-Raman modes should be checked going forward, and neutron/x-ray scattering spectroscopy should be measured to reveal what happens at non-zero q. It is well known that phonons behave differently at different momenta, so it is very possible that a mode at non-zero q could play a role in CMR. From our measurements, the $q = 0$ optical phonons are rigid under magnetic field [Supplementary Fig. 6]. We added a note to this effect in the main text.

Referee 1 writes: *(5) Why is H_0 frequency-dependent, is such a behavior seen in other CMR materials with electronic inhomogeneity?*

Our reply: In our approach, H_0 describes the field at which the carriers in $Mn_3Si_2Te_6$ start to exhibit long-range connectivity. It plays a role analogous to concentration in a more traditional percolation approach. Certainly different percolation thresholds have been seen in various manganites and rare earth compounds. The surprise here is that in $Mn_3Si_2Te_6$, the carriers do not respond evenly to the magnetic field. In this work, we show that the low frequency carriers respond promptly to low magnetic fields whereas the higher frequency carriers are more sluggish (and require a higher driving force). As a result, H_0 is frequency-dependent. Based upon our literature search, this approach to understanding electronic heterogeneity (where H controls the carriers and then the carriers display percolation behavior) is an extension of existing models and can be considered a new direction. Thanks for noticing.

Referee 1 writes: *Minor issues: Several terms should be explained: 'gap sequence', line 91; 'strong electronic features', line 92; 'oscillator strength' (what oscillator?), line 133; 'a new bound state' (what bound state?), line 188. S2 on line 160 is stated to be 'measured values of . . . ', is it measured or a fit parameter? The 'full field' seems to be above the experimentally accessible limit.*

Our reply: Fixed. The changes are highlighted in blue.

Response to Reviewer 2:

Referee 2 writes: *The team investigates the magneto-optical properties of $Mn_3Si_2Te_6$, a nodal-line semiconductor, which has garnered much research attention in the recent past, owing to the occurrence of unusual CMR. This work attempts to shed additional light on such an unusual CMR effect by performing infrared spectroscopic measurements as a function of temperature and magnetic fields. The main discovery is the field-driven insulator-to-metal transition, which leads to a weakly metallic state with localized carriers. The percolation model provided evidence for electronic inhomogeneity and phase separation.*

Our reply: Nicely summarized, thank you!

Referee 2 writes: *These results are quite encouraging in the growing field of van der Waals magnetic materials and their emerging properties. The optical (reflectance) properties of this compound as a function of temperature and magnetic field have not been reported. I strongly believe that this work is original.*

Our reply: Thank you so much for the strong endorsement!

Referee 2 writes: *While this manuscript sounds quite rich in interpretation and analysis,*

its quality can be further improved by addressing the following comments.

Our reply: We welcome constructive feedback and modifications to improve the quality of our work.

Referee 2 writes: *1. From my perspective, it is quite useful to independently support the evidence for the presence of inhomogeneities and phase separation.*

Our reply: This is an excellent suggestion. Near field infrared imaging could (in principle) visualize the proposed electronic inhomogeneity in $Mn_3Si_2Te_6$ and be a "silver bullet" test for phase separation. The challenge is to perform the work at 4.2 K and 17 T. There are a few research teams developing this capability but to our knowledge none have it operational. This type of infrared imaging will be an important extension to our magneto-infrared spectroscopy - once it is available. Meanwhile, we need to take advantage of other methods to explore the localized electronic excitation in $Mn_3Si_2Te_6$. Examples include microwave and second harmonic generation imaging. Real space ARPES or x-ray imaging might also be helpful. Clearly, our work is only the first step in addressing this question. We added additional text in the discussion to emphasize this point.

Referee 2 writes: *2. It is important to provide the materials characterization details such as XRD, XPS, etc to gain confidence in the quality of the crystals used for the measurements reported here.*

Our reply: Yes, good idea. We relied extensively on Raman scattering to gain confidence in the quality of our $Mn_3Si_2Te_6$ crystals [Fig. 1**a** below]. In response to Referee 2's request, we added an entire section [Supplementary Note 1] to the Supplemental Information detailing exactly how this technique works and what we find under different circumstances. This may be important because unlike transport measurement, Raman scattering spectroscopy is not already shown extensively in the literature. We also added x-ray characterization [Fig. 1**b** below] of our crystals. Unfortunately, we do not have XPS in our lab. That said, all characterization in Supplementary Note 1 support the high quality of our sample during measurements.

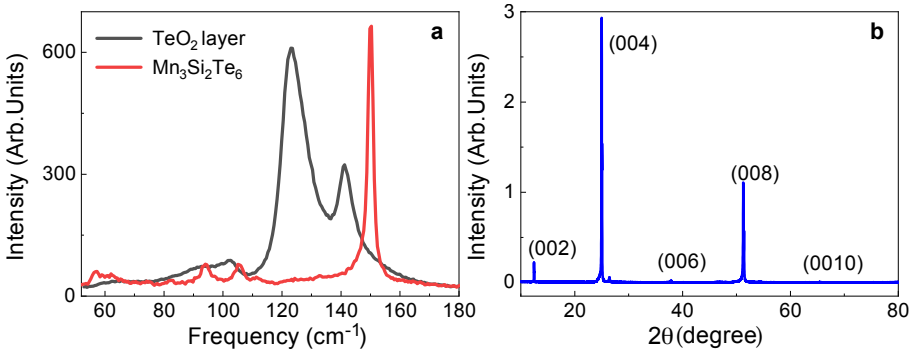

FIG. 1. **a** Raman response of $Mn_3Si_2Te_6$ and TeO_2 layers at room temperature. **b** XRD pattern collected along $(00l)$ direction.

Referee 2 writes: *3. It would be beneficial for the community to provide basic magnetic characterization to show the ferrimagnetic phase transition temperature.*

Our reply: Yes, we measured magnetization for characterization purposes and are happy to include it in the Supplementary Note 1. As illustrated in Fig. 2 below, the ferrimagnetic phase transition temperature is similar to that reported in other studies.

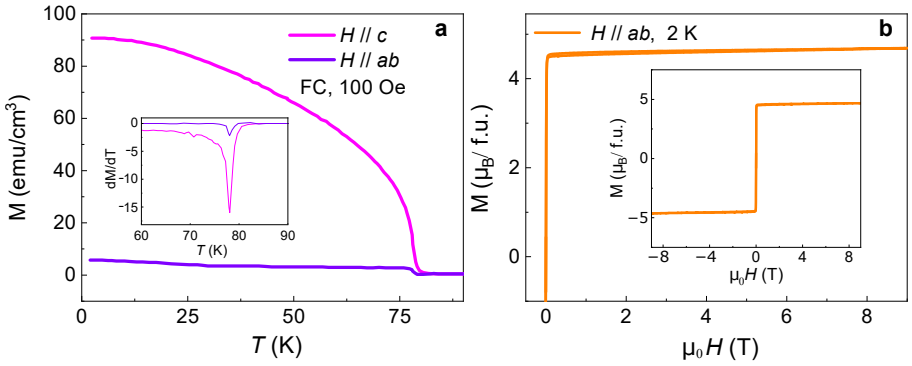

FIG. 2. **a** Temperature dependent magnetization of $Mn_3Si_2Te_6$. **b** Magnetic field dependence of magnetization at $T = 2$ K.

Referee 2 writes: *4. This compound is known to show competing magnetic phases due to inequivalent Mn sites. One wonders if this is considered in the data analysis and interpretation.*

Our reply: This is an interesting question. The $Mn^{(1)}$ and $Mn^{(2)}$ sites are distinct in terms of the phonons, but as we learn from this work, none of the infrared-active phonons are sensitive to the magnetic field-induced insulator-to-metal transition. This makes the distinction a lot less interesting. How $Mn^{(1)}$ and $Mn^{(2)}$ contribute to the electronic response is still an open question. Theory may be best suited for revealing site- and symmetry-selective information about the high field "metallic" phase of $Mn_3Si_2Te_6$. The size of the metallic droplets grows or diminishes depending on the magnetic field, so it is unlikely that there is a simple 1 to 1 correspondence between $Mn^{(1)}$ and $Mn^{(2)}$ sites although there may be different types of carriers with different mobilities. To check for that possibility, we reexamined our projected density of states calculations. As we see from Fig. 3 below, the $Mn^{(1)}$ and $Mn^{(2)}$ states reside at similar energies. Spin-polarized transport or ARPES measurements could presumably distinguish the $Mn^{(1)}$ vs. $Mn^{(2)}$ contributions, as they have opposite momentum directions [Phys. Rev. B 107, 054430 (2023)], but an optical properties measurement probably can not differentiate their contributions.

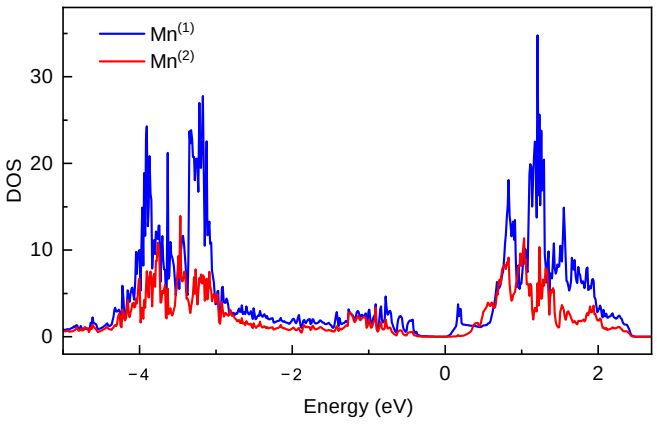

FIG. 3. It's not so surprising that $Mn^{(1)}$ and $Mn^{(2)}$ have similar density of states: each hosts a 2+ valence state, a d^5 configuration, and an octahedral environment. For each unit cell, there are 4 $Mn^{(1)}$ and 2 $Mn^{(2)}$, so that the total DOS of $Mn^{(1)}$ is larger than that of $Mn^{(2)}$.

Referee 2 writes: *5. Compounds like this tend to form a layer of TeO_2 on its surface. Have the authors considered the contribution coming from this layer while analyzing the data?*

Our reply: Referee 2 is correct that the presence of TeO_2 has a dramatic impact on the results, and we agree that it's an excellent idea to illustrate the consequences. It turns out that Raman scattering easily identifies the presence of TeO_2 [Supplementary Note 1]. We therefore polished and checked for TeO_2 contamination before each measurement using Raman scattering spectroscopy and can confirm that there was no TeO_2 layer on the surface. To further inform the interested reader of the consequences, we added Supplementary Note 2 to show how the infrared response changes due to TeO_2 contribution in an "aged" sample [Fig. 4 below].

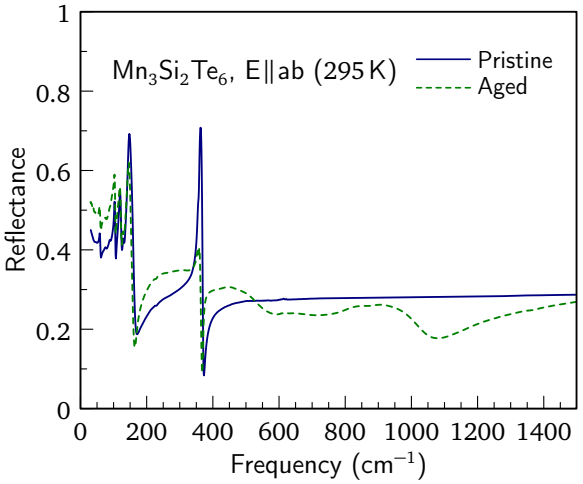

FIG. 4. The reflectivity of a freshly-grown, pristine sample of $Mn_3Si_2Te_6$ single crystal for light polarized in the *ab* planes at room temperature in the far- and mid-infrared regions (solid line), compared with the reflectivity of the same sample after having been stored in an air desiccator for several months (dashed line); there are significant changes in the reflectivity levels and the line shape of the high-frequency infrared-active mode.

Response to Reviewer 3:

Referee 3 writes: *$Mn_3Si_2Te_6$ is a compound that has attracted significant attention within the scientific community due to its unusual properties. The authors have made a substantial contribution towards understanding the insulator-to-metal transitions in this material. However, before recommending publication, the authors should address a few issues:*

Our reply: Thank you for your interest!

Referee 3 writes: *1. Appropriate error bars should be added in the main text and supplementary data, for example, in Figure 2 and Figure 4.*

Our reply: Yes, many of the error bars are smaller than the symbol size, but there are a few that are larger - for instance in Fig. 2d and Fig. 4c. To improve their visibility, we changed the style and color of the error bars and added additional text to the figure captions.

Referee 3 writes: *2. An anharmonicity model was used in Figure 2 for the analysis of the phonon energy temperature dependence. Why did the authors not consider lattice thermal*

expansion effects?

Our reply: Indeed, Referee 3 is correct that the change in phonon frequency with temperature is not entirely due to anharmonic coupling but also thermal expansion. Although thermal expansion itself occurs as a result of anharmonicity, it affects the quasi-harmonic frequencies through the harmonic force constant. The temperature dependence of phonon frequency can be modeled by Eq. 1 from Refs. Phys. Rev. B 97, 054306 (2018), Phys. Rev. B 90, 024411 (2014), which describes contributions from both the anharmonic decay and lattice thermal expansion.

$$\omega(T) = \omega_0 \left[1 - \gamma \frac{V(T) - V_0}{V_0} - \left(\frac{\Gamma_{L,0}}{\sqrt{2}\omega_0} \right)^2 \left(1 + \frac{4\lambda_{\text{ph-ph}}}{\exp\left(\frac{\hbar\omega_0}{2k_B T} \right) - 1} \right) \right] \tag{1}$$

$V(T)$ and V_0 are the volumes of the unit cell at varying temperatures T and $T \to 0$, respectively, obtained from Ref. Phys. Rev. B 95, 174440 (2017). γ is the Grüneisen parameter, $\Gamma_{L,0}$ and ω_0 are the linewidth and frequecny at the zero temperature limit, and $\lambda_{\text{ph-ph}}$ is the phonon-phonon coupling. These are free parameters in the fitting of Eq. 1 and the fitted curves (dotted lines) are shown below.

Comparing the anharmonicity model used in the main text with the model that includes both anharmonic decay and lattice thermal expansion (Eq. 1), the extracted ω_0 values are very close in both models [Table 1, below], which yields similar spin-phonon coupling constants. As the fitted Grüneisen parameters are small and consistent with the Ref. New J. Phys. 25 103020 (2023), we conclude that the thermal expansion effect can be ignored in our estimation of the spin-phonon coupling constant. In other words, it's the order of magnitude of the spin-phonon coupling that matters, and in this case, it turns out that adding this additional complexity to the model does not change the physics.

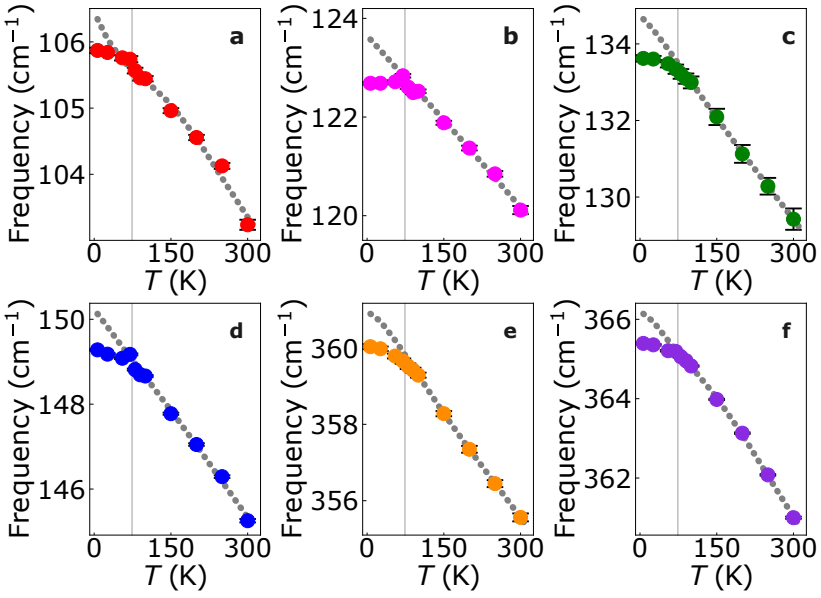

FIG. 5. **a-f** Frequency vs. temperature for six representative phonons. Individual points are obtained from fits to $\sigma_1(\omega)$ in panel Fig. 2**a**, and the dotted lines represent a fit of Eq. 1, which contains contributions from both the anharmonic decay and the lattice thermal expansion effect. The magnetic ordering temperature is indicated by the gray vertical line.

Sym.	ω_0 (cm^{-1}) from anharmonicity model	ω_0 (cm^{-1}) from lattice thermal expansion model
E_u	105.7	106.4
E_u	123.5	123.6
E_u	135.0	134.7
E_u	150.0	150.2
E_u	361.4	360.9
E_u	366.2	366.2

TABLE I. Comparison of ω_0 from two different models.

Referee 3 writes: *3. Can you comment on the 150 cm^{-1} phonon evolution around 150 K? Did you observe something similar as reported in Phys. Rev. B 107, 054309?*

Our reply: Yes, the phonon near 150 cm^{-1} has an unusual shape. We tried the model from Ref. Phys. Rev. B 107, 054309 (2023), which involves the convolution of the Fano and Gaussian functions. An example of the fitting is shown below. We tested four temperatures (6.5, 80, 150, and 300 K) with Voigt profiles indicated in cyan and the line shapes resulting from the convolution of the Fano + Gaussian functions marked in red. These approaches give fittings that are almost the same and overlap strongly. Although the line shapes between Voigt and the convolution of the Fano + Gaussian functions are very close, the absolute values of the Fano parameter q at 80 K ($|q|$=5000, constrained) and 150 K ($|q|$=5000, constrained) are much larger than those at 6.5 K ($|q|$=93) and 300 K ($|q|$=100), which might indicate the presence of magnetic correlations reported in Ref. Phys. Rev. B 107, 054309 (2023).

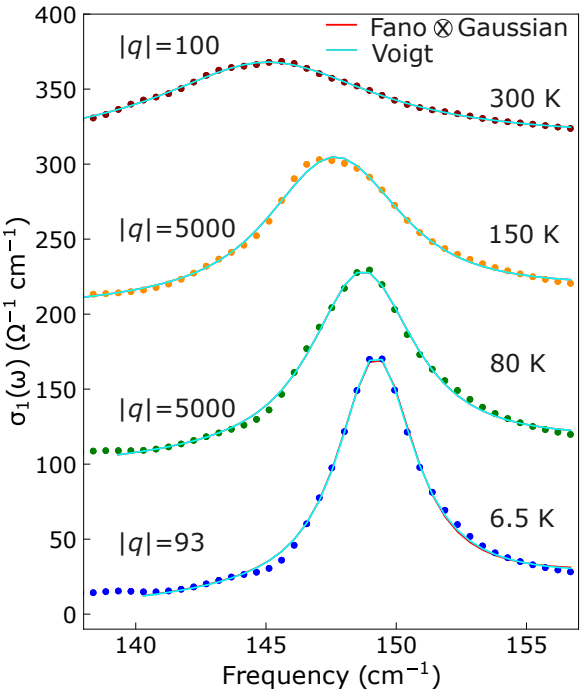

FIG. 6. Optical conductivity as a function of temperature. The circles represent the experimental data, which are offset for clarity. The red solid lines represent the line shape obtained as a convolution of Fano + Gaussian profiles, whereas the cyan solid lines represent Voigt profiles. The red and cyan solid lines overlap almost completely.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

The authors have made considerable efforts to address the reviewers' concerns, in my view the responses are satisfactory, I therefore recommend this work for publication.

Reviewer #2 (Remarks to the Author):

The revised manuscript satisfactorily addressed my comments as well as other reviews. I believe this is worthy of publication in Nature Communications. I encourage the team to proofread the manuscript before it gets published.

Reviewer #3 (Remarks to the Author):

The author addressed all the comments satisfactorily. It is my great pleasure to recommend the manuscript for publication.

Response to Reviewer 1:

Referee 1 writes: *The authors have made considerable efforts to address the reviewers' concerns, in my view the responses are satisfactory, I therefore recommend this work for publication.*

Our reply: We appreciate the time and effort you invested in reviewing our manuscript. Thank you very much!

Response to Reviewer 2:

Referee 2 writes: *The revised manuscript satisfactorily addressed my comments as well as other reviews. I believe this is worthy of publication in Nature Communications. I encourage the team to proofread the manuscript before it gets published.*

Our reply: Thank you for recommending our manuscript for publication. The manuscript has been thoroughly proofread by multiple individuals.

Response to Reviewer 3:

Referee 3 writes: *The author addressed all the comments satisfactorily. It is my great pleasure to recommend the manuscript for publication.*

Our reply: Thank you for recommending our manuscript for publication. We appreciate your support and feedback throughout the review process.