



January 2023

Pressure - temperature phase diagram of CrSiTe₃

J L. Musfeldt
musfeldt@utk.edu

David Mandrus
University of Tennessee, Knoxville

Zhenxian Liu
University of Illinois Chicago, zliu@bnl.gov

Follow this and additional works at: https://trace.tennessee.edu/utk_chempubs

 Part of the [Condensed Matter Physics Commons](#), and the [Materials Chemistry Commons](#)

Recommended Citation

Musfeldt, J L.; Mandrus, David; and Liu, Zhenxian, "Pressure - temperature phase diagram of CrSiTe₃" (2023). *Chemistry Publications and Other Works*.
https://trace.tennessee.edu/utk_chempubs/66

This Article is brought to you for free and open access by the Chemistry at TRACE: Tennessee Research and Creative Exchange. It has been accepted for inclusion in Chemistry Publications and Other Works by an authorized administrator of TRACE: Tennessee Research and Creative Exchange. For more information, please contact trace@utk.edu.

Insulator-metal transition in CrSiTe₃ triggered by structural distortion under pressure

J. L. Musfeldt,^{1,2,*} D. G. Mandrus,^{3,4} and Z. Liu⁵

¹*Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, USA*

²*Department of Physics and Astronomy,
University of Tennessee, Knoxville, Tennessee 37996, USA*

³*Department of Materials Science and Engineering,
University of Tennessee, Knoxville, Tennessee 37996, USA*

⁴*Materials Science and Technology Division,
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

⁵*Department of Physics, University of Illinois Chicago, IL 60607-7059, USA*

(Dated: January 16, 2023)

Abstract

van der Waals solids are well known to host remarkable phase diagrams with competing phases, unusual energy transfer processes, and elusive states of matter. Among this class of materials, chalcogenides have emerged as the most flexible and relevant platforms for unraveling charge-structure-function relationships. In order to explore the properties of complex chalcogenides under external stimuli, we measured the far infrared spectroscopic response of CrSiTe₃ under extreme pressure-temperature conditions. Analysis of the 368 cm⁻¹ Si-Te stretching mode and the manner in which it is screened by the closure of the indirect gap reveals that the insulator-metal transition takes place immediately after the structural phase transition - once the mixed phase aspect of the lattice distortion is resolved. At the same time, the two-phase region associated with the structural transition widens with decreasing temperature, and the slope of the insulator-metal transition under pressure is consistent with increasing entropy. These trends completely revise the character of the temperature-pressure phase diagram as well as the relationship between the structural and insulator-metal transitions, leading to a critical nexus of activity that may hide a quantum critical point and allow superconductivity to emerge.

* musfeldt@utk.edu

Complex chalcogenides are exceptionally responsive to external stimuli. Under compression, systems like CrSiTe_3 , FePS_3 , MnPS_3 , and CrGeTe_3 host layer sliding, insulator-metal transitions, magnetic dimensionality crossovers, piezochromism, the possibility of orbital-selective Mott and polar metal states, and superconductivity [1–22]. The 33 K ferromagnet CrSiTe_3 has earned widespread recognition for remarkable properties in both single crystal and monolayer form [23–27]. The discovery of pressure-induced superconductivity above 7.5 GPa and below 4.2 K is one of these exciting developments [23]. Establishing the local lattice distortions and the precise relationship between the structural and insulator-metal transitions is crucial to unraveling how superconductivity develops and distinguishing between conventional vs. unconventional mechanisms in this class of materials. At the same time, CrSiTe_3 is a layered van der Waals material that has attracted extraordinary attention for the demonstration of single-layer ferromagnetism and current-driven control of the spin state [27–34]. Whether superconductivity arises in the ultrathin limit is currently unexplored, although the fact that the Curie temperature T_C rises with decreasing layer number as well as under strain and pressure [30, 31, 33] suggests that the superconducting transition temperature might do so as well [35, 36]. Further developing the phase diagram and resolving the connection between the structural and insulator-metal transitions as well as the intersection of competing phases is a significant step toward evaluating such a relationship.

In order to explore these themes in a complex chalcogenide, we combined synchrotron-based infrared spectroscopy and diamond anvil cell techniques to measure the far infrared response of CrSiTe_3 under extreme pressure-temperature conditions. Because closing an indirect gap screens the phonons much less effectively than closing a direct gap, we can follow the evolution of the phonons into the metallic state. The 2E_u symmetry Si-Te stretching mode at 368 cm^{-1} - noteworthy for engaging in spin-phonon coupling across the magnetic ordering transition [24] - is particularly informative in this regard. This vibrational mode hardens strongly on approach to the pressure-driven structural transition, broadens and develops weak doublet character in the mixed-phase region, and rides on top of a gradually increasing electronic background as the indirect gap begins to close. In the end, the insulator-metal transition is swift and sharp. What differentiates our work from previous results is

58 the finding that the first-order structural phase transition in CrSiTe_3 is triggered before
59 (but in close proximity to) the insulator-metal transition. The latter is set in motion almost
60 immediately afterwards. With decreasing temperature, the two-phase region associated with
61 the structural transition broadens, and the insulator-metal transition shifts to slightly higher
62 pressure, indicative of a positive entropy change. Our findings run counter to previous results
63 [23] and completely revise the entire character of the temperature - pressure ($T - P$) phase
64 diagram for this compound. These trends also open the possibility that the juxtaposition of
65 events both hides a quantum critical point and lays the foundation for superconductivity.

66 RESULTS AND DISCUSSION

67 Spectroscopic signatures of the structural and insulator-metal transitions

68 Figure 1(a) displays the infrared response of CrSiTe_3 at ambient conditions inside the
69 diamond anvil cell. Three infrared-active vibrational modes are observed. We assign the
70 peak near 90 cm^{-1} as an A_u symmetry Te displacement mode, the feature near 215 cm^{-1} as
71 an 1E_u symmetry Te-Cr-Te bending mode, and the peak at 368 cm^{-1} as a 2E_u symmetry
72 Si-Te stretching mode. All of these features harden significantly under pressure. In order
73 to understand the local lattice distortions associated with the structural phase transition,
74 we track the frequency shifts and splittings of these phonons as a function of pressure.
75 The behavior of the Si-Te stretching mode determines the location of the structural phase
76 transition. We find that weak doublet character signals a mixed phase region that persists
77 over a broad pressure range [Fig. 1(c)]. Oscillator fits of the Si-Te phonon reveal where the
78 process begins and ends. The insulator-metal transition is different. Due to the superior
79 stability and brightness of the synchrotron source, we can measure absorption very close to
80 the metallic transition - even though the signal is low - and we can follow the entire transition
81 into the metallic phase because CrSiTe_3 is a bad metal with an indirect gap. As an additional
82 check, we monitor the emerging metallicity with complementary reflectance spectroscopy.
83 Both techniques provide similar estimates of the critical pressure for the insulator-metal
84 transition.

85 **Sequence of pressure-driven transitions in CrSiTe₃ at room temperature**

86 The behavior of the 368 cm⁻¹ Si-Te stretching mode is particularly revealing [Fig. 1(b,c)].
87 In addition to hardening strongly under pressure ($\partial\omega/\partial P = 3.4$ cm⁻¹/GPa at 300 K), the Si-
88 Te stretch broadens considerably between approximately 6 and 8 GPa and displays a poorly
89 resolved doublet structure. Oscillator fits of these structures are shown in the Supporting
90 information. This broadening and eventual peak separation could be a signature of (i) weak
91 symmetry breaking or (ii) a mixed phase regime. There are two pieces of evidence that point
92 toward the latter scenario. First, the character of the frequency vs. pressure plot in Fig. 1(c)
93 is consistent with phase coexistence. Second, the x-ray diffraction data of Cai *et. al.* provide
94 clear evidence for a sluggish structural phase transition between $R\bar{3}$ and a high pressure phase
95 over the same range [23]. We therefore attribute the broadening and subsequent weak doublet
96 character of the Si-Te stretching mode to the simultaneous presence of two slightly different
97 structural phases between approximately 6 and 8 GPa. CrSiTe₃ therefore goes from $R\bar{3} \rightarrow$ a
98 two phase region that is a combination of $R\bar{3} +$ the high pressure phase \rightarrow a high pressure
99 phase that is slightly different from $R\bar{3}$. The mixed phase regime is relatively narrow at room
100 temperature, and the subsequent high pressure structure does not last long in isolation. In
101 fact, the appearance of this phase almost immediately triggers the insulator-metal transition.
102 Based upon room temperature x-ray diffraction [23], the structure of the high pressure and
103 metallic phases are probably the same. A similar scenario in terms of transition primacy
104 plays out in FePS₃ [16].

105 Metallicity in CrSiTe₃ develops gradually at room temperature. The absorption back-
106 ground rises with increasing pressure, and the phonons rise partially screened above it until
107 the 0.4 eV indirect gap closes, completely obscuring the phonons [Fig. 1(d)]. This definition
108 of the onset to the insulator-metal transition is consistent with the gradual maturation of
109 metallicity in the reflectance spectra as well. Tracking the development of metallicity in this
110 manner is a much better way to determine the location of the insulator-metal transition than
111 from an inflection point or “hump” in the resistivity [23]. The “hump method” might work
112 for a direct gap material, but closure of the indirect gap in CrSiTe₃ is more subtle. In our
113 hands, the indirect gap is fully closed, and metallicity is established at 9.5 GPa. We reiterate
114 that it is very clear that the 0.4 eV indirect gap is closing - not the 1.2 eV direct gap [24],

115 because the latter does not move into our frequency window. This makes the system a bad
116 metal. Closure of a direct gap would likely be sharp and strong. There would be no chance of
117 seeing phonons after metallicity sets in due to screening effects. Indirect gap closure, on the
118 other hand, is a very favorable situation, giving a beautiful view of the structural transition
119 and gradual evolution of metallicity. **Direct gap closure takes place at higher pressure.**

120 **Tracking these transitions to lower temperatures**

121 CrSiTe₃ hosts a similar pattern of phonons at lower temperatures, and the three infrared-
122 active vibrational modes get sharper due to lifetime effects. The two-phase region (consisting
123 of $R\bar{3}$ and a higher pressure phase with slightly different structure) broadens considerably
124 and becomes more sluggish with decreasing temperature. Metallicity appears only after the
125 structural phase transition is complete - typically near 9.5 GPa. At 100 K, the insulator-
126 metal transition is above 10 GPa, indicating that the phase boundary is moving outward.
127 The trend is even stronger at 50 K [Fig. 2], and the mixed phase persists over a wider
128 pressure range than before. Even so, the structural phase transition is always complete
129 before the insulator-metal transition takes place and once it is resolved, metallicity arises
130 almost immediately. Each step is an independent process, and the sequence is invariably the
131 same: $R\bar{3} \rightarrow$ mixed phases \rightarrow high pressure structural phase \rightarrow insulator-metal transition.
132 This progression is exactly opposite of what is reported in Ref. [23].

133 The space group in the narrow high pressure region between the structural phase transition
134 and the insulator-metal transition is also of interest. Unfortunately, the phonons are heavily
135 screened in this bad metal region, making it difficult to analyze symmetry breaking and carry
136 out a subgroup analysis [20, 22]. We can, however, state that the high pressure vibrational
137 properties of CrSiTe₃ above the two-phase region are inconsistent with the $R\bar{3}$ space group
138 that has been proposed for CrGeTe₃ [7] because the infrared spectra of CrSiTe₃ provides no
139 evidence for a loss of the inversion center which is expected for a transition to a polar space
140 group. Clearly more effort is needed to reveal the symmetry and properties of CrSiTe₃ above
141 the structural phase transition.

142 **Developing the temperature-pressure phase diagram**

143 Figure 3 displays the $T - P$ phase diagram of CrSiTe_3 , created by bringing together
144 spectroscopic information about the structural and insulator-metal transitions described
145 above with selected data on the pressure dependence of the Curie and superconducting
146 transition temperatures from Ref. 23. The overall character of the phase diagram is quite
147 different from the previous report [23] especially in terms of the sequence of the structural
148 and insulator-metal phase transitions and the shape of the phase boundaries. In our hands,
149 the structural transition is initiated and fully complete before the insulator-metal transition
150 takes place, and metallicity is due to closure of the indirect gap. We know that the direct
151 gap is still open at 10 GPa because we do not see it come into our spectral range at these
152 pressures. **Closure of the direct gap takes place at higher pressure.**

153 As indicated on the $T - P$ phase diagram, the insulator-metal phase boundary occurs
154 after the structural phase transition - not before - and it moves to higher pressure with
155 decreasing temperature. Therefore the slope of $\partial T/\partial P$ is negative rather than positive as
156 previously supposed [23]. From a thermodynamic point of view, this means that changes
157 in volume and entropy have opposite signs. Since the volume change ΔV is likely ≤ 0
158 under compression, the change in entropy ΔS is probably ≥ 0 [38]. In other words, entropy
159 increases across the insulator-metal transition. Similar trends are observed in 1T-TiSe₂ [39].
160 By contrast, the two-phase region of the structural phase transition broadens with decreasing
161 temperature. That the mixed phase region is larger at low temperatures might be due to
162 non-hydrostaticity, but it is more likely a consequence of the first order transition exhibiting
163 a wider hysteresis. Even so, the structural phase transition is much more involved in the
164 development of superconductivity than previously believed. At the lowest temperatures that
165 we could reach while still increasing pressure *in-situ*, both the structural and insulator-metal
166 transitions occur in quick succession and seem to be in very close proximity to a number
167 of competing states including superconductivity. This intersection of states suggests that a
168 quantum critical point may reside in the vicinity. While we can not say anything specific
169 about the superconducting state in CrSiTe_3 , we now better understand the sequence of events
170 leading up to superconductivity. In fact, it may turn out that the insulator-metal transition
171 directly triggers superconductivity at low temperature.

173 To summarize, we measured the far infrared response of CrSiTe_3 under extreme pressure-
174 temperature conditions in order to reveal how pressure controls the interplay between the
175 structural phase transition, the insulator-metal transition, ferromagnetism, and supercon-
176 ductivity in a complex chalcogenide. We find that the insulator-metal transition is triggered
177 by the structural phase transition almost immediately - once the sluggish mixed-phase region
178 is eliminated. Furthermore, the structural transition widens with decreasing temperature,
179 and the slope of the insulator-metal transition is consistent with increasing entropy. These
180 trends change completely the character of the $T - P$ phase diagram and lead to a critical
181 nexus of activity that may hide a quantum critical point and allow superconductivity to
182 emerge at low temperature. Because of this work, we better understand how the different
183 phases of CrSiTe_3 develop on approach to superconductivity.

184 Extension of the $T - P$ phase diagram toward the few- and single-sheet limit is highly
185 desirable. There is already evidence in other systems such as FeSe and TaS_2 that the su-
186 perconducting transition temperature T_C increases in the ultrathin limit [35, 36]. Here, it is
187 important to use a technique that can accurately identify closure of the indirect gap. As we
188 discuss, *dc* conductivity is not very good for establishing the insulator-metal transition in
189 CrSiTe_3 , but it should be ideal for identifying the superconducting transition. Infrared tech-
190 niques by contrast are superb for tracking the structural and insulator-metal transitions in
191 CrSiTe_3 but will probably be less successful following the transition to the superconducting
192 state. In principle, infrared spectroscopy can see the gap open (if the system is *s*-wave), but
193 it will be challenging to see a superconducting gap develop inside a diamond anvil cell at
194 low temperature and in the ultra-thin limit. Techniques based upon relative slope changes
195 in the reflectance may be successful if electron-phonon processes are relevant [40]. Beyond
196 unraveling the sequence of transitions that trigger superconductivity in CrSiTe_3 , the ability
197 to control complex chalcogenides under pressure will advance the science base and support
198 the development of high-performance photoresponsive devices and efficient hydrogen storage
199 [41, 42].

METHODS

High quality CrSiTe₃ single crystals were grown via flux techniques as described previously [24]. A small, well-shaped piece of the crystal was selected and loaded into a suitably-chosen diamond anvil cell with a hydrocarbon grease (petroleum jelly) pressure medium to assure quasi-hydrostatic pressure conditions and an annealed ruby ball to determine pressure via fluorescence [37]. The synthetic type IIa diamonds in the symmetric diamond anvil cell had 500 μm culets, and we employed a 47 μm thick pre-indented stainless steel gasket with a 200 μm hole diameter. Care was taken to optimize optical density in order to reveal the features of interest. Taking advantage of the stable, high-brightness beam, synchrotron-based infrared spectroscopy (60-680 cm^{-1} ; 4 cm^{-1} resolution; both transmittance and reflectance geometries) was performed using the 22-IR-1 beamline at the National Synchrotron Light Source II at Brookhaven National Laboratory. Absorbance is calculated as $\alpha(\omega) = -\ln(\mathcal{T}(\omega))$, where $\mathcal{T}(\omega)$ is the measured transmittance. Pressure was increased between 0 and 11 GPa - first at room temperature and then at several lower temperatures using a custom-built cryostat that accomodates the diamond anvil cell and supports *in-situ* compression measurements. For the low temperature experiments, one ruby ball was positioned inside the sample chamber while another was placed on the diamond backplate as a temperature reference [37]. We also monitored the shape of the ruby fluorescence spectrum to assure that the sample remained in a quasi-hydrostatic environment. Although an open flow system, this cryostat is limited to work above approximately 50 K in order to control the step size during isothermal compression of the diamond anvil cell. Our protocol for determining the position of each phase transition was developed at room temperature (as described in the Supporting information) and then extended to low temperature. The phase transitions are fully reversible upon release of pressure at each temperature. **Further, recompression of the same crystal and then release gives the same results, so we can be confident that crystal quality remains high under these extreme pressure-temperature conditions.**

DATA AVAILABILITY

Data are available from the corresponding author upon reasonable request.

228 **ACKNOWLEDGEMENTS**

229 JLM appreciates funding from Physical Behavior of Materials, Basic Energy Sciences,
230 U.S. Department of Energy (Contract number DE-SC00023144). DM acknowledges support
231 from the Gordon and Betty Moore Foundation’s EPiQS Initiative, Grant GBMF9069. Work
232 at the National Synchrotron Light Source II at Brookhaven National Laboratory is funded by
233 the Department of Energy (DE-AC98-06CH10886). Use of the 22-IR-1 beamline is supported
234 by COMPRES, the Consortium for Materials Properties Research in Earth Sciences, under
235 NSF Cooperative Agreement EAR 1606856 and CDAC (DE-NA0003975). We thank S. N.
236 Neal, K. Park, and K. A. Smith for useful conversations.

237 **AUTHOR CONTRIBUTIONS**

238 JLM designed the study. DM grew the crystals. JLM and ZL performed the high pressure
239 measurements. JLM analyzed the spectral data and wrote the manuscript. All authors
240 commented on the text.

241 **COMPETING INTERESTS**

242 The authors declare no competing interests.

-
- 243 [1] Zallen, R., Effect of pressure on optical properties of crystalline As_2S_3 , *High Pres. Res.* **24**,
244 117 (2004).
245 [2] Wang, Y. *et. al.*, Pressure-driven cooperative spin-crossover, large-volume collapse, and
246 semiconductor-to-metal transition in manganese(II) honeycomb lattices, *J. Am. Chem. Soc.*
247 **138**, 15751 (2016).
248 [3] Haines, C. *et. al.*, Pressure-induced electronic and structural phase evolution in the van der
249 Waals compound FePS_3 , *Phys. Rev. Lett.* **121**, 266801 (2018).
250 [4] Wang, Y. *et. al.*, Emergent superconductivity in an iron-based honeycomb lattice initiated by
251 pressure-driven spin-crossover, *Nat. Commun.* **9**, 1914 (2018).

- 252 [5] Coak, M. J. *et. al.*, Isostructural Mott transition in 2D honeycomb antiferromagnet $V_{0.9}PS_3$,
253 *npj Quant. Mater.* **4**, 38 (2019).
- 254 [6] Zheng, Y., Jiang, X. X., Xue, X. X., Dai, J., & and Feng, Y., *Ab initio* study of pressure-driven
255 phase transition in $FePS_3$ and $FePSe_3$, *Phys. Rev. B* **100**, 174102 (2019).
- 256 [7] Yu, Z. *et. al.*, Pressure-induced structural phase transition and a special amorphization phase of
257 two-dimensional ferromagnetic semiconductor $Cr_2Ge_2Te_6$, *J. Phys. Chem. C* **123**, 13885–13891
258 (2019).
- 259 [8] Kim, H. S., Haule, K., & Vanderbilt, D., Mott metal-insulator transitions in pressurized
260 layered trichalcogenides, *Phys. Rev. Lett.* **123**, 236401 (2019).
- 261 [9] Wang, X. *et. al.*, Current-driven magnetization switching in a van der Waals ferromagnet
262 Fe_3GeTe_2 , *Sci. Advances* **5**, eaaw8904 (2019).
- 263 [10] Susilo, R. A. *et. al.*, Band gap crossover and insulator-metal transition in the compressed
264 layered $CrPS_4$, *npj Quantum Materials* **5**, 58 (2020).
- 265 [11] Coak, M. J. *et. al.*, Tuning dimensionality in van-der-Waals antiferromagnetic Mott insulators
266 $TMPS_3$, *J. Phys.: Condens. Matter* **32** 124003 (2020).
- 267 [12] Harms, N. C. *et. al.*, Piezochromism in the magnetic chalcogenide $MnPS_3$, *npj Quant. Mater.*
268 **5**, 56 (2020).
- 269 [13] Kang, S. *et. al.*, Coherent many-body exciton in van der Waals antiferromagnet $NiPS_3$, *Nature*
270 **583**, 785-789 (2020).
- 271 [14] Ma, X. *et. al.*, Dimensional crossover tuned by pressure in the layered magnetic $NiPS_3$, *Sci.*
272 *China Phys. Mech. Astron.* **64**, 297011 (2021).
- 273 [15] Wildes, A. R. *et. al.*, High field magnetization of $FePS_3$, *Phys. Rev. B* **101**, 024415 (2020).
- 274 [16] Coak, M. J. *et. al.*, Emergent magnetic phases in pressure-tuned van der Waals antiferromagnet
275 $FePS_3$, *Phys. Rev. X* **11**, 011024 (2021).
- 276 [17] Kim, M., Kim, H. -S., Haule, K, & Vanderbilt, D., Orbital-selective Mott phase and non-Fermi
277 liquid in $FePS_3$, *Phys. Rev. B* **105**, L041108 (2022).
- 278 [18] Zhu, F. F. *et. al.*, Topological magnon insulators in two-dimensional van der Waals ferromag-
279 nets $CrSiT_3$ and $CrGeTe_3$: Toward intrinsic gap-tunability, *Sci. Advances* **7**, eabi7532 (2021)
- 280 [19] Mai, T. T. *et. al.*, Magnon-phonon hybridization in 2D antiferromagnet $MnPSe_3$, *Sci. Advances*
281 **7**, eabj3106 (2021).

- 282 [20] Harms, N. C. *et. al.*, Symmetry progression and polar metallicity in NiPS₃ under pressure, *npj*
283 *2D Materials and Applications* **6**, 40 (2022).
- 284 [21] Zhao, H. *et. al.* Mechanical control of physical properties in the van der Waals ferromagnet
285 Cr₂Ge₂Te₆ via application of electric current, *Phys. Rev. B*, **106**, L041103 (2022).
- 286 [22] Harms, N. C. *et. al.* Metal site substitution and the role of the P–P dimer on symmetry
287 breaking in FePS₃ and CrPS₄, *ACS Appl. Elect. Mater.* **4**, 3246 (2022).
- 288 [23] Cai, W. *et. al.*, Pressure-induced superconductivity and structural transition in ferromagnetic
289 CrSiTe₃, *Phys. Rev. B* **102**, 144525 (2020).
- 290 [24] Casto, L. D. *et. al.*, Strong spin-lattice coupling in CrSiTe₃, *Appl. Phys. Lett. Materials* **3**,
291 041515 (2015).
- 292 [25] Williams, T. J. *et. al.*, Magnetic correlations in the quasi-two-dimensional semiconducting
293 ferromagnet CrSiTe₃, *Phys. Rev. B* **92**, 144404 (2015).
- 294 [26] Liu, B. *et. al.*, Critical behavior of the quasi-two-dimensional semiconducting ferromagnet
295 CrSiTe₃, *Sci. Rep.* **6**, 33873 (2016).
- 296 [27] Gong, C. *et. al.*, Discovery of intrinsic ferromagnetism in two-dimensional van der Waals
297 crystals, *Nature* **546**, 265-269 (2017).
- 298 [28] Lebegue, S., Bjorkman, T., Klintenberg, M., Nieminen, R., & Eriksson, O., Two-dimensional
299 materials from data filtering and ab initio calculations, *Phys. Rev. X* **3**, 31002 (2013).
- 300 [29] Li, X. & Yang, J., CrXTe₃ (X = Si, Ge) nanosheets: two dimensional intrinsic ferromagnetic
301 semiconductors, *J. Mater. Chem. C* **2**, 7071-7076 (2014).
- 302 [30] Chen, X., Qi, J., & Shi, D., Strain-engineering of magnetic coupling in two-dimensional mag-
303 netic semiconductor CrSiTe₃: Competition of direct exchange interaction and superexchange
304 interaction, *Phys. Lett. A* **379**, 60-63 (2015).
- 305 [31] Lin, M. -W. *et. al.*, Ultrathin nanosheets of CrSiTe₃: a semiconducting two-dimensional fer-
306 romagnetic material, *J. Mater. Chem. C* **4**, 315-322 (2016).
- 307 [32] Zhang, J. -M., Nie, Y. -Z., Xia, Q. -L., Xiong, R. & Guo, G. -H., Electronic structures and
308 magnetic properties of CrSiTe₃ single-layer nanoribbons, *Phys. Lett. A* **383**, 2346-2351 (2019).
- 309 [33] Zhang, C. *et. al.*, Pressure-enhanced ferromagnetism in layered CrSiTe₃ flakes, *Nano Lett.* **21**,
310 7946-7952 (2021).

- 311 [34] Ron, A. *et. al.*, Ultrafast enhancement of ferromagnetic spin exchange induced by ligand-to-
312 metal charge transfer, *Phys. Rev. Lett.* **125**, 197203 (2020).
- 313 [35] Navarro-Moratalla, E. *et. al.*, Enhanced superconductivity in atomically thin TaS₂, *Nature*
314 *Commun.* **7**, 11043 (2016).
- 315 [36] Shigekawa, K. *et. al.*, Dichotomy of superconductivity between monolayer FeS and FeSe, *Proc.*
316 *Nat. Acad. Sci.* **116**, 24470 (2019).
- 317 [37] Mao, H. K., Bell, P. M., Shaner, J. W., & Steinberg, D. J., Specific volume measurements of
318 Cu, Mo, Pd, and Ag and calibration of the ruby R₁ fluorescence pressure gauge from 0.06 to
319 1 Mbar, *J. Appl. Phys.* **49** 3276 (1976).
- 320 [38] Smith, K. A. *et. al.*, Revealing pressure-driven structural transitions in the hybrid improper
321 ferroelectric Sr₃Sn₂O₇, *Phys. Rev. B* **104**, 064106 (2021).
- 322 [39] Kusmartzeva, A. F., Sipos, B., Berger, H., Forró, L., & Tutis, E., Pressure induced supercon-
323 ductivity in pristine 1T-TiSe₂, *Phys. Rev. Lett.* **103**, 236401 (2009).
- 324 [40] Carbotte, J. P., Nicol, E. J., & Timusk, T., Detecting superconducting in the high pressure
325 hydrides and metallic hydrogen from optical properties, *Phys. Rev. Lett.* **121**, 047002 (2018).
- 326 [41] Ramos, M. *et. al.*, Ultra-broad spectra photo-response in FePS₃ air stable devices, *npj 2D*
327 *Mater. and Appl.* **5**, 19 (2021).
- 328 [42] Rezaie, A. A., Lee, E., Luong, D., Yapo, J. A., & Fokwa, B. P. T., Abundant active sites
329 on the basal plane and edges of layered van de Waals Fe₃GeTe₂ for highly efficient hydrogen
330 evolution, *ACS Mater. Lett.* **3**, 313 (2021).

FIGURE LEGENDS

FIG. 1. (a) Infrared spectrum of CrSiTe_3 inside the diamond anvil cell at 300 K. Based upon an $R\bar{3}$ space group, this van der Waals material hosts three infrared-active phonon modes. The 368 cm^{-1} Si-Te stretching mode is strongly coupled to the 33 K ferromagnetic ordering transition [24]. Inset: calculated displacement pattern for the Si-Te stretching mode at 368 cm^{-1} reproduced from Ref. 24. This displacement modulates the Te centers in the 90° Cr-Te-Cr superexchange pathway. (b) Close-up view of the Si-Te stretching mode showing the development of the first-order structural phase transition, the rising absorption background, and metallicity. (c) Frequency vs. pressure plot of the Si-Te stretching mode at room temperature. The closed and open symbols correspond to two different runs. The mixed phase region associated with the structural phase transition is indicated in gray. Inset: close-up view of the Si-Te stretch showing the development of doublet character due to the presence of two coexisting phases. (d) Spectral evidence for the insulator-metal transition due to closure of the indirect gap near 9.55 GPa (indicated in gray). The spectra are on an absolute scale; they are not shifted in any way. Complementary reflectance data is shown in the Supporting information.

FIG. 2. (a) Close-up view of the infrared-active Si-Te stretching mode showing the development of the first-order structural phase transition. The two-phase region becomes more sluggish with decreasing temperature. Oscillator fits are available in the Supporting information. (b) Spectral evidence for the insulator-metal transition due to closure of the indirect gap. The background is rising, and the phonons rise incompletely screened on top of the metallic background until the indirect gap closes and the signature of the phonons disappears due to screening by the Drude (indicated in gray). These spectra are on an absolute scale; they are not shifted in any way.

FIG. 3. Temperature - pressure phase diagram summarizing the structural, magnetic, and electronic properties of CrSiTe_3 . The beginning and end of the structural phase transition as well as the position of the insulator-metal transition are determined from the spectroscopic results discussed here. The Curie temperature and the superconducting transition temperature ($\times 5$) as a function of pressure are from Ref. 23.