Observation of a massive phason in a charge-density-wave insulator

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The lowest-lying fundamental excitation of an incommensurate charge-density-wave material is believed to be a massless phason—a collective modulation of the phase of the charge-density-wave order parameter. However, long-range Coulomb interactions should push the phason energy up to the plasma energy of the charge-density-wave condensate, resulting in a massive phason and fully gapped spectrum. Using time-domain terahertz emission spectroscopy, we investigate this issue in (TaSe4)2I, a quasi-one-dimensional charge-density-wave insulator. On transient photoexcitation at low temperatures, we find the material strikingly emits coherent, narrowband terahertz radiation. The frequency, polarization and temperature dependences of the emitted radiation imply the existence of a phason that acquires mass by coupling to long-range Coulomb interactions. Our observations underscore the role of long-range interactions in determining the nature of collective excitations in materials with modulated charge or spin order.

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The fundamental collective modes (amplitudon and phason) of a broken-symmetry ordered state (Fig. 1a) have been key in establishing foundational theories across various fields of physics, including gauge theories in particle physics, as well as superconductors, antiferromagnets and charge-density-wave (CDW) materials in condensed-matter physics. The phason is typically massless, in accordance with Goldstone’s theorem, which necessitates the emergence of a massless boson for broken symmetry in systems where the ground or vacuum state is continuously degenerate. A prominent exception occurs in superconducting systems. Here, even though the ground state is continuously degenerate, the long-range Coulomb interaction pushes the longitudinal phonon branch around the CDW wavevector \( q_{\text{CDW}} \) (Fig. 1b). Below the CDW transition temperature \( T_{\text{CDW}} \), this mode softening results in the linear-in-wavevector, zero-gap dispersion of the phason, implying that the CDW can freely slide for excitation wavevector \( q = 0 \). In any real material, however, random impurities and disorder restrict this sliding motion, leading to a small gap in phason dispersion (pinning frequency) (Fig. 1b). Thus, the sliding CDW motion can only be observed if a strong enough electric field is applied to first depin the phason. The resulting sliding motion of the CDW can then be measured in d.c. transport experiments as done in various systems.

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However, the above phenomenology of a massless phason (or disorder pinned phason at low frequency) assumes the absence of long-range Coulomb interactions \( U \). This assumption is believed to be valid because the presence of normal electrons at a non-zero temperature can screen \( U \). However, if \( U \) is sufficiently strong or if the density of normal electrons is sufficiently low, then the CDW phason at \( \mathbf{q} = 0 \) should be pushed to higher energies (even above the amplitude energy) (Fig. 1c). This behaviour was highlighted in work on CDW dynamics and then formalized in a later work that noted the similarity of the emergence of a massive CDW phason with the Anderson–Higgs mechanism in a superconductor. Later works predicted that the massive (optical) phason could indeed dominate over the massless (acoustic) phason at sufficiently low temperatures where charged quasiparticles cannot sufficiently screen \( U \). Within these models, the amplitude remains unaffected by the long-range Coulomb interaction. We note that in superconductors, the plasma frequency is much larger than the single-particle gap, rendering the phase mode unobservable deep in the superconducting phase. In a CDW system, however, the relevant scale is the plasma frequency of the condensate, which can lie far below the single-particle gap. To date, direct experimental evidence of a massive phason in CDW systems has been elusive.

Here we present the evidence for the generation and detection of a massive phason in the CDW insulator \((\text{TaSe}_4)_2\text{I}\), a quasi-one-dimensional (quasi-1D) material that undergoes an incommensurate CDW transition below \( T_{\text{CDW}} = 260 \, \text{K} \) (refs. 9–11) with a CDW gap for single-particle excitations of \( 2\Delta_{\text{CDW}} = 250–300 \, \text{meV} \) (refs. 12–14). \((\text{TaSe}_4)_2\text{I}\) is unique among quasi-1D CDW systems due to its unusually high resistivity in the low-temperature insulating state (Supplementary Information), such that the long-range Coulomb interaction can remain unscreened and the massive phason can have substantial spectral weight. To investigate the collective modes of the CDW order in \((\text{TaSe}_4)_2\text{I}\), we performed time-domain terahertz (THz) emission spectroscopy using an ultrafast photoexcitation ‘pump’ pulse with an energy of \( 1.2 \, \text{eV} \) (\( \lambda = 1.030 \, \text{nm} \)) (Fig. 2a shows the experimental geometry and Supplementary Information provides further details of the experimental setup). Note that the photoexcitation energy here is greater than \( 2\Delta_{\text{CDW}} \), and therefore, the pump pulse initially creates single-particle excitations across the CDW gap. As \((\text{TaSe}_4)_2\text{I}\) is structurally chiral (space group 97) and lacks inversion symmetry, this photoexcitation generates a transient current with a duration of a few picoseconds (ps). Such a phenomenon is well known as a photogalvanic or a photo-Dember effect, both of which can occur in systems lacking inversion symmetry\(^6\). The transient current then results in a short ps-duration burst of THz radiation in the far field, which we measure in the time domain using standard electro-optical sampling (Supplementary Information).

Figure 2b shows the measured time profile of the THz electric field \( E_{\text{THz}}(t) \) emitted from \((\text{TaSe}_4)_2\text{I}\) on photoexcitation at \( T = 7 \, \text{K} \ll T_{\text{CDW}} \). Here the pump is \( p \)-polarized, with an electric-field component along the quasi-1D chains of \((\text{TaSe}_4)_2\text{I}\). Two features are immediately evident in \( E_{\text{THz}}(t) \): a transient peak around \( t_{\text{delay}} = 0 \, \text{ps} \) followed by a long-lived coherent oscillation that lasts over ~80 ps. In the frequency domain (Fig. 2b, inset), the transient peak around \( t_{\text{delay}} = 0 \, \text{ps} \) manifests as a broad distribution over frequencies from 0.1 to 2.0 THz, whereas the long-lived coherent oscillation manifests as a sharp peak centred at 0.23 THz. For the rest of this work, we refer to the transient \( E_{\text{tr}} \) and the coherent oscillation as \( E_{\text{osc}} \). As noted above, \( E_{\text{tr}} \) is what we typically expect from such an experiment due to the photogalvanic or photo-Dember effect. The transient current can be estimated from the measured \( E_{\text{tr}} \), and is greater than the current necessary to depin the dynamics of the CDW order in \((\text{TaSe}_4)_2\text{I}\) (Supplementary Information).

We focus on the observed narrowband THz emission \( E_{\text{osc}} \) since this aspect of the data is particularly striking. Here \( E_{\text{osc}} \) lasts well over 80 ps—much longer than the typical few-ps-duration signal expected from semiconductors\(^1\) and semimetals\(^2\)–\(^4\) in THz emission experiments. Another unusual feature of \( E_{\text{osc}} \) is the observed waveform envelope in the time domain, which appears to gradually increase in magnitude starting at \( t_{\text{delay}} = 0 \, \text{ps} \). In impulsive excitation ultrafast experiments, the signal is usually peaked at \( t_{\text{delay}} = 0 \, \text{ps} \) from where it exponentially decays. Additionally, although the measured transient peak \( E_{\text{tr}} \) is both horizontally and vertically polarized, the coherent oscillation \( E_{\text{osc}} \) is only horizontally polarized (Fig. 2c). In our experimental geometry, this corresponds to \( E_{\text{osc}} \) being polarized along the quasi-1D chains of \((\text{TaSe}_4)_2\text{I}\) (Fig. 2a).

To investigate the origin of the radiating mode, we study the \( E_{\text{osc}} \) spectra at different temperatures (Fig. 3a,b). The \( E_{\text{osc}} \) signal is the strongest at 7 K and gradually decreases with increasing temperature, showing a sudden drop at ~80 K (at about 30% of \( T_{\text{CDW}} \)). This feature is also clear in the integrated spectral weight of the 0.23 THz mode as a function of temperature (Fig. 3c). Note that the initial transient signal, \( E_{\text{tr}} \), is similar at both 70 and 100 K, but the oscillating mode \( E_{\text{osc}} \) is considerably weaker at 100 K. To further understand the origin of the radiating mode, we studied the dependence of \( E_{\text{osc}} \) on the incident pump fluence (Fig. 3d–f). The spectral shape of \( E_{\text{osc}} \) does not change with a decreasing pump fluence—only the overall spectral weight linearly decreases with decreasing fluence (Fig. 3f), indicating that we are in a perturbative regime.
Fig. 2 | THz emission from (TaSe₄)₂I. 

a. Geometry of the sample orientation, incident light (pump) and emitted THz polarizations. TaSe₄ chains (c axis) are oriented along the z axis, and the pump beam is p polarized with incident angle \( \theta_i = 45^\circ \). The plane of incidence is represented as the grey-shaded region.

b. THz emission signal \( E_{THz} \) as a function of time \( t_{delay} \), measured at 7 K. The Fourier-transform amplitude \( A_{FT} \) is plotted in the inset. The 0.23 THz mode is marked with an asterisk (*).

c. The p- and s-polarized components of the THz emission signal are \( E_{p}^{THz} \) (top) and \( E_{s}^{THz} \) (bottom), respectively. \( E_{p}^{THz} \) is shown with an offset.

Fig. 3 | Temperature \( T \) and pump fluence \( F \) dependence of the 0.23 THz mode. 

a. THz emission signal as a function of delay time at a few select temperatures. The signals at different temperatures are offset for clarity.

b. Fourier transforms of the traces shown in a. c. Spectral weight (SW) of the 0.23 THz mode as a function of temperature, normalized to the SW value at 7 K. The dashed line indicates \( 0.3T_{CDW} = 80 \) K.

d. THz emission signal at 7 K as a function of delay time at a few select pump fluences. The signals at different fluences are shown with offsets for clarity.

e. Fourier transforms for the traces shown in d.

f. SW of the 0.23 THz mode as a function of pump fluence, normalized to the maximum value of SW. The normalized SW in c and f are obtained by integrating the Fourier transforms \( A_{FT}(\omega) \) of \( E_{osc}(t) \) over a 0.05-THz-wide frequency window centred at 0.23 THz. The error bars in the normalized SW are determined by Fourier transforming \( E_{osc}(t) \) over two different time windows (with widths of 10 and 50 ps).
Based on the observations above, we can rule out several possible sources for the radiating mode at 0.23 THz, such as the phonon gap due to pinning disorder \(^1\), optical phonons \(^2\), longitudinal acoustic phonons \(^3\) or CDW amplitude. Pinning is trivially ruled out since the measured phonon gap due to disorder in (TaSe\(_4\))\(_2\)I is around 0.03 THz (ref. \(^1\); Supplementary Section 4.6), that is, nearly an order of magnitude smaller than the 0.23 THz oscillation measured in our work. The lowest-frequency optical phonons in (TaSe\(_4\))\(_2\)I are at much higher frequencies (1.1 THz \(^4\)), whereas quasi-particles and the long-range Coulomb interaction penalizes the spatial modulation of charge density. This causes the acoustic-mode phase velocity to increase with decreasing temperature. Once the temperature becomes sufficiently low such that the renormalized phason velocity is faster than the quasi-particle velocity, screening is no longer effective and the Coulomb interaction gaps the phase mode via the Anderson–Higgs mechanism, yielding the massive phason (Supplementary Fig. 8). By using typical values for the ionic mass of quasi-1D CDW compounds and including dynamical screening effects, previous work \(^5\) estimated the failure of screening to begin around \(T = 0.3T_{\text{CDW}}\). Taken together, our observations strongly suggest that the narrowband 0.23 THz radiation originates from the predicted massive phason in a CDW insulator.

To determine the excitation mechanism for the massive phason, we further discuss the temporal waveform of \(E_{\text{osc}}\) highlighted earlier. Note that \(E_{\text{osc}}\) shown in Fig. 2b is roughly zero at \(t_{\text{delay}} = 0\) ps and then becomes notable only at later times. We fit the behaviour of \(E_{\text{osc}}\) in time using a model of two coupled modes, one of which is excited at \(t_{\text{delay}} = 0\) ps, whereas only the other one radiates (Fig. 4) (Supplementary Information provides details on the fitting procedure). This fitting model is consistent with a picture where the radiating mode is the massive phason with frequency \(\omega_{\text{ph}}\), whereas the non-radiating mode is a zone-folded acoustic phonon with wavevector \(\vec{q} = \vec{q}_{\text{CDW}}\) for \(T > T_{\text{CDW}}\) and frequency \(\omega_{\text{ph}} = \omega_{\text{ph}}\). The presence of such an acoustic mode was established elsewhere \(^6\). Given that the infrared pump excites a large number of single-particle excitations above the CDW gap, we hypothesize that the zone-folded acoustic phonon is coherently excited via either a displacive excitation of coherent phonons mechanism \(^7\) or the pressure of a non-equilibrium distribution of quasi-particles \(^8\). Both these mechanisms result in the maximum phonon amplitude at \(t_{\text{delay}} = 0\) ps (Fig. 4). Once excited, the acoustic phonon can scatter off the CDW modulation and excite the massive phason mode. The massive phason mode at \(\vec{q} = 0\) will then radiate, explaining the time profile of \(E_{\text{osc}}\) (Figs. 3 and 4).

To conclude, we note that (TaSe\(_4\))\(_2\)I was recently argued to be an axion insulator (in the presence of an external magnetic field) based on magnetoconductance measurements of the sliding phonon dynamics \(^9\), although such an interpretation is under active debate \(^10\). Since (TaSe\(_4\))\(_2\)I is a good insulator at low temperatures (Supplementary Information), the reported magnetoconductance measurements \(^11\) were limited to temperatures above 80 K. Our results imply that at low temperatures, long-range Coulomb interactions are crucial for a full understanding of the CDW order in (TaSe\(_4\))\(_2\)I and related axion insulator candidates. Contributions to the longitudinal magnetoconductance due to axion electrodynamics may occur near the massive phason frequency, which can coherently provide a promising way to manipulate axionic states. Furthermore, our methodology here can provide a direct dynamical probe of collective excitations and effects of long-range interactions.
in materials with modulated order parameters such as spin or pair density waves.

**Online content**

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41563-023-01504-5.

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Methods
Single crystals of (TaSe₄)₂I were prepared using chemical vapour transport. Stoichiometric amounts of Ta wire (99.9%), Se powder (99.999%) and I shot (99.99%) were loaded into a fused silica tube, which was sealed under a vacuum and heated with a source temperature of 600 °C and sink temperature of 500 °C for 10 days. X-ray diffraction patterns were collected on a Bruker D8 ADVANCE diffractometer with Mo Kα radiation. Resistivity was measured in the four-point geometry in a Quantum Design physical property measurement system. The (110) surface of (TaSe₄)₂I was oriented using backscattering Laue diffraction.

THz emission spectroscopy was performed with our custom-built time-domain THz spectroscopy setup based on a Yb:KGW amplifier laser (PHAROS, LIGHT CONVERSION). The fundamental laser pulse wavelength is 1.030 nm with a pulse duration of ~160 fs. The fundamental beam is split into pump and probe paths using a 90:10 beam-splitter. The pump fluence ranged between 70 and 580 μJ cm⁻² with a 1/e² width of ~1 mm. The pump was incident onto the sample at a 45° angle of incidence. The sample was kept inside a closed-cycle cryostat with He exchange gas (SHI-950, Janis Research). The THz field E_{THz}(t) radiated by the sample is collected by an off-axis parabolic mirror and focused on a CdTe (110) crystal. The electro-optical sampling probe beam is made to spatially and temporally overlap with E_{THz}(t) on the CdTe crystal for electro-optic sampling. The path length of the probe is adjusted with a delay stage to control the time delay (t_{delay}). The quasi-1D chain of (TaSe₄)₂I was oriented to lie in the plane of incidence for all the measurements in this work.

Data availability
Source data are provided with this paper. Additional data are available from the corresponding author upon reasonable request.

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Author contributions
S.K., Y.L., N.B., A.M. and F.M. performed the THz emission spectroscopy experiments and the corresponding data analysis. X.-Q.S. and B.B. developed the theoretical understanding and modelling. C.Z., K.Q. and D.P.S synthesized and characterized the samples. R.A.D., Q.L.D.N. and M.T. gave crucial insights into the understanding and analysis of the data. S.K., X.-Q.S., B.B. and F.M. wrote the manuscript with input from all the authors. F.M. conceived and supervised this project.

Competing interests
The authors declare no competing interests.

Additional information
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