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Decompression-Driven Superconductivity Enhancement in In_2Se_3

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An unexpected superconductivity enhancement is reported in decompressed In_2Se_3. The onset of superconductivity in In_2Se_3 occurs at 41.3 GPa with a critical temperature (T_c) of 3.7 K, peaking at 47.1 GPa. The striking observation shows that this layered chalcogenide remains superconducting in decompression down to 10.7 GPa. More surprisingly, the highest T_c that occurs at lower decompression pressures is 8.2 K, a twofold increase in the same crystal structure as in compression. It is found that the evolution of T_c is driven by the pressure-induced *R*-3*m* to *I*-43*d* structural transition and significant softening of phonons and gentle variation of carrier concentration combined in the pressure quench. The novel decompression-induced superconductivity enhancement implies that it is possible to maintain pressure-induced superconductivity at lower or even ambient pressures with better superconducting performance.

High-pressure superconductivity investigation has been shown to be of paramount significance for understanding the physical mechanisms of superconductivity, searching for new superconductors, and promoting superconducting critical temperature (T_c),[1–8] as exemplified by the recently published study of compressed sulfur hydride system, a conventional superconductor that lies outside the limitation of 40 K and has the highest T_c achieved to date.[1,2,9] A long-term pursuit or challenge is how to preserve the superconductivity achieved by pressure approach to low and even ambient pressure,[2–7] and thus promote the practical application of pressure-induced superconductors. Superconductivity enhancement if possible in pressure quenching, would of course be more desirable.

For this study, we chose layered In_2Se_3, one of two-dimensional (2D) chalcogenides as the candidate material for a step study toward this goal. The 2D electronic structures of these materials can be modulated by external pressure, and usually their pressure-modulated modifications exhibit irreversible character during decompression,[8,10–12] which could be beneficial for achieving pressure-quenchable superconductivity. Besides, In_2Se_3 is considerably sensitive to the external conditions. It shows extremely large electronic anisotropy between in-plane and cross-plane conductivity, and large resistance variation between different electronic states with varying external conditions.[13–21] Desired electronic structure can be thus tuned. Furthermore, the pressure-driven 2D–3D structural crossover in In_2Se_3 is quite different from the transition of other layered chalcogenide materials,[10–12,19–21] indicating the unusual variation of electronic states. We carried out the electrical transport measurements on single crystalline In_2Se_3 during compression and decompression cycles, complemented by X-ray diffraction (XRD) experiments to monitor the structural evolution.

The electrical transport measurements show that In_2Se_3 goes through a semiconducting–metallic transition at ≈9.1 GPa (Figure S1 and S2, Supporting Information), and remains metallic upon further compression. At 41.3 GPa and 3.7 K, the resistance drops sharply. This drop becomes more noticeable

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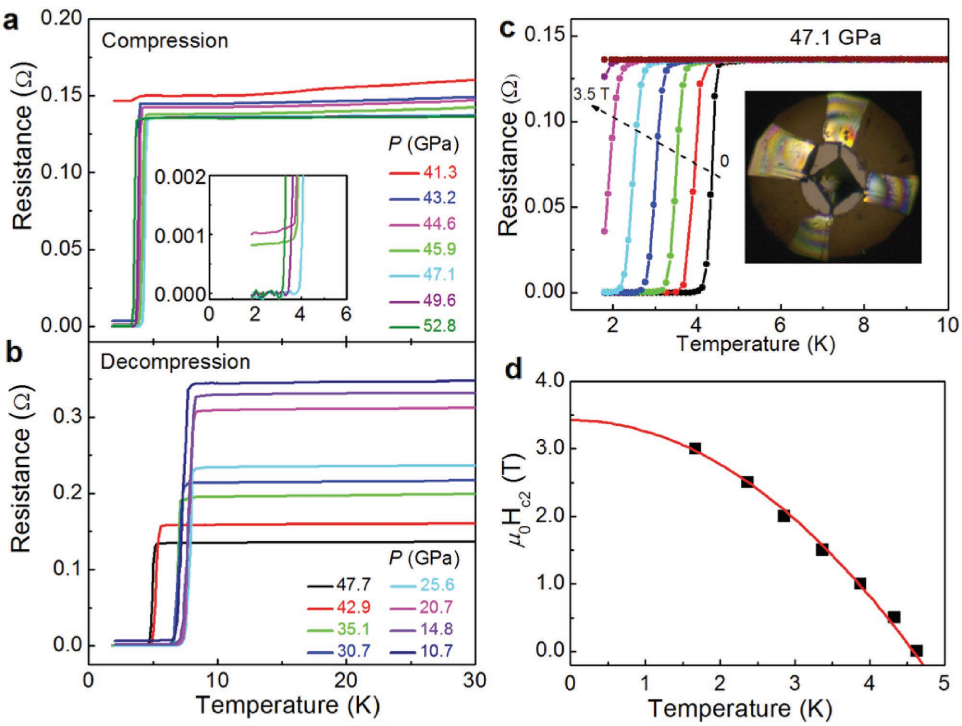

Figure 1. Evidence for pressure-driven superconductivity in In_2Se_3. The temperature-dependent resistance at representative pressures in compression a and b) decompression runs, respectively. c) Temperature-dependent resistances at various magnetic fields from 0.0 to 3.5 T. The inset shows the microphotography of the layered In_2Se_3 at 52.8 GPa for electrical transport measurements. d) The temperature dependence of superconducting critical field. The curve was extrapolated using the $H_c(T) = H_{c0}(1 - (T/T_c)^2)$ formula for the estimation of H_c.

with increasing pressure (**Figure 1**a). Zero electrical resistance is observed at ≈47.1 GPa, indicating the superconducting behavior of In_2Se_3. By suppressing the superconducting phase with various external magnetic fields (Figure 1c), the zero-resistance state shifts toward lower temperatures gradually with increasing magnetic fields, and a field of 3.5 T almost completely suppresses the superconducting state of In_2Se_3. The magnetic susceptibility examinations confirm the superconducting behaviors and bulk superconductivity characters (Figure S4, Supporting Information).

Figure 2 summarizes the evolution of T_c in compression and decompression cycles. The superconducting behavior of In_2Se_3 first occurs at 41.3 GPa with T_c = 3.7 K. The highest T_c of 4.6 K was measured at 47.1 GPa during the entire compression. A striking observation is that, with quenching pressure from 52.8 GPa (Figure 1b), this layered chalcogenide remains superconducting in decompression to 10.7 GPa, which is about 30 GPa lower than the onset pressure of superconductivity in compression. Also, surprisingly in the decompression runs, T_c increases considerably with releasing pressure. The highest T_c of ≈8.2 K occurs at the lower decompression pressures, which is about twofold of the T_c achieved in the compression. After the disappearance of superconductivity, we repressurized In_2Se_3 up to 43.8 GPa and then quenched to ambient pressure. The significant enhancement of T_c in decompression can be repeated consistently. In another experimental cycle with the highest uploading pressure of 45.3 GPa (lower than the pressure of highest T_c in compression, 47.1 GPa) shown in Figure 2b, T_c first increases with compression from 40.7 to 45.3 GPa. However, in decompression, T_c does not follow the reverse trend of compression and does not go back to its original values, but keeps the upward trend with releasing pressure and the highest T_c achieved in decompression is almost double that achieved in compression. After decompression down to 11.5 GPa, we recompressed In_2Se_3 up to 43.0 GPa and then quenched to ambient pressure. All the results show better repeatability with the above pressure cycles. Our experimental results clearly demonstrate an exciting scenario of decompression-driven superconductivity enhancement.

Usually, pressure compression has a reversible modulation on superconductors, i.e., the evolution of T_c in decompression follow the reverse trend in compression and pressure-induced superconductivity often fade away or disappear with releasing pressure.[1–7] In sharp contrast to those old observations, a twofold increase in T_c of decompressed In_2Se_3 compared to that in compression process is really surprising. To understand why it occurs, we firstly examine the possible correlation with Se, which has been proved to be superconducting under pressure.[22–24] Our electrical transport measurements show that the T_c of Se varies differently from that of In_2Se_3 in the pressure cycle (Figure S5, Supporting Information), so the relevance can be excluded.

To investigate the structural cause, we carried out in situ high-pressure XRD measurements for structural characterization (**Figure 3**a). With compression up to 35.6 GPa, a new structure takes form, and the structural transition completes above 46.3 GPa. The high-pressure phase remains stable up to the highest pressure of this study (52.8 GPa). The diffraction

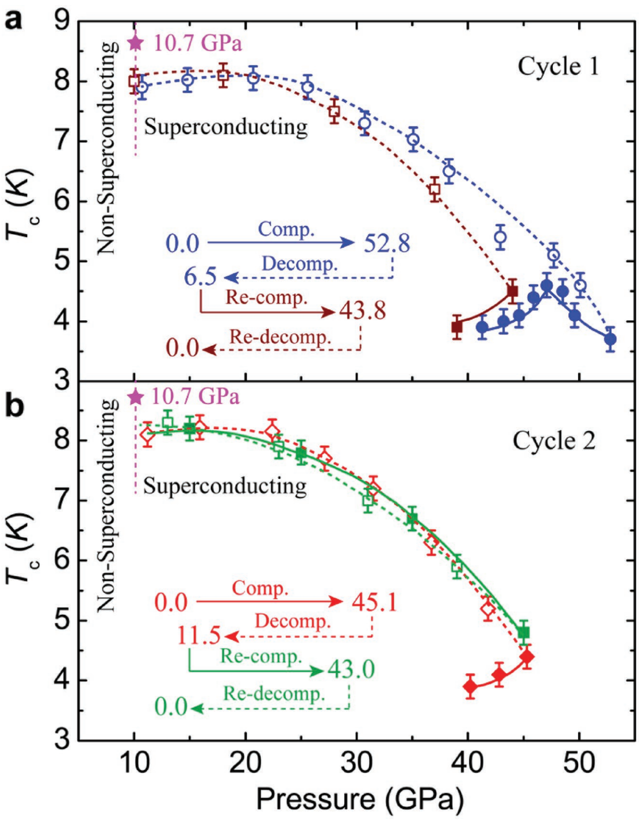

Figure 2. a and b) The evolution of superconducting temperature, T_c, in different pressure cycles. The closed and open symbols represent the compression and decompression data, respectively. The solid and dotted lines are a guide for the eye.

pattern of the high-pressure phase remains unchanged when the sample is quenched to ambient pressure, indicating that the high-pressure phase is quenchable. For the starting phase, the diffraction patterns of In_2Se_3 below 35.6 GPa can be well indexed into a rhombohedral structure.[19,20] Based on the Rietveld refinement with GSAS software (Figure 3b), the high-pressure phase is found to have a body-centered cubic structure. The structure can be better identified with *I*-43*d* symmetry, in which the $InSe_8$ dodecahedron is partially overlapped with the $SeIn_6$ octahedron, consistent with a recently reported study.[21] More structural information is shown in Supporting Information. The quenchable high-pressure phase may be due to the 2D–3D structural crossover in In_2Se_3 under compression. Previous studies showed that Ln_2Se_3 (Ln = lanthanide elements) with smaller Ln cation usually crystallizes into six-coordinated face-centered orthorhombic structure,[25–27] similar to the *R*-3*m* structure of In_2Se_3,[21] whereas Ln_2Se_3 with larger Ln cation usually adopts the cubic phase, isostructural with the high-pressure phase of In_2Se_3.[21,25,28,29] Their structural similarity can also be viewed from the mean (d_{M-Se}) and difference (Δd_{M-Se}) of two nonequivalent M–Se distances at ambient pressure for cubic M_2Se_3 (M = In and Ln elements).[21] Furthermore, previously reported results indicate that Se is more compressible than In,[30,31] i.e., the atomic radii ratio (r_{In}/r_{Se}) increases with pressure, so we speculate that the structural transition of In_2Se_3 may arise from the changes in atomic radii of In and Se in compression. Further experimental study is needed for direct verification.

To study the electron density of state at the Fermi surface, $N(E_F)$, as well as the electron–phonon coupling of In_2Se_3 in pressure cycles, we carried out Hall effect experiments at 20 K and various pressures. As shown in **Figure 4**, the carrier concentration of In_2Se_3 increases significantly with pressure from 41.3 to 47.1 GPa, where T_c rises with pressure. Upon further compression, the variation of carrier concentration flattens, while T_c changes its pressure dependence and decreases obviously with increasing pressure. An unexpected observation is that the carrier concentration remains almost unchanged with pressure quenching down to 10.7 GPa, which favors the T_c enhancement in decompression.

Previous studies indicated that the onset of superconductivity was usually accompanied with a structural transition. For instance, in Bi_2X_3 (chemically and structurally isostructural with In_2Se_3), the superconducting phase emerges followed by a rhombohedral-monoclinic structural transition.[32,33] In our experiments, the onset of superconductivity in In_2Se_3 was also associated with the rhombohedral-cubic structural transition. In the decompression process, the cubic structure remains unchanged, which maintains the high-pressure electronic structure and further the superconducting state until below 10.7 GPa. Therefore, it is reasonable to conclude that the high-pressure cubic phase is responsible for the emergence of superconductivity in In_2Se_3, but the superconductivity enhancement in In_2Se_3 is not a consequence of structural transition in decompression.

According to the BCS and Mcmillan–Allen–Dynes theories,[34,35] when the electron–phonon coupling (λ) is strong enough to overcome the Coulomb repulsion (μ), electrons form "Cooper pairs", resulting in the emergence of superconductivity. Coulomb repulsion is usually material insensitive,[36] but electron–phonon coupling may vary with materials or structures as:

$$\lambda = N\left(E_F\right) D^2 / M \omega_{ph}^2 \tag{1}$$

where $N(E_F)$ is the electron density of state at the Fermi level, and D is the deformation potential, and M and ω_{ph} are the effective atomic mass and phonon frequency, respectively. The increasing electron density of state at the Fermi surface $N(E_F)$ usually enhances electron–phonon coupling and hence T_c. Conversely, T_c can be suppressed by the pressure-induced phonon stiffening, as shown in MgB_2.[32,37] In the case of In_2Se_3, from 41.3 to 47.1 GPa, T_c was promoted with the increasing carrier concentration in the compression, indicating their correlation. Upon further compression above 47.1 GPa, the carrier concentration changes very little, and some other factors, such as phonon stiffening, win out to change the evolution of T_c. It seems that these two contrary mechanisms (the carrier concentration and phonon strength) mainly determine how the T_c changes in pressurized In_2Se_3.

Pressure compression usually results in phonon stiffening, which is responsible for the drop of T_c above 47.1 GPa. In contrast, phonon softening occurs due to decompression, and the carrier concentration remains almost unchanged at the level of its maximum until below 10.7 GPa. This results in the enhancement of T_c, reaching the highest T_c

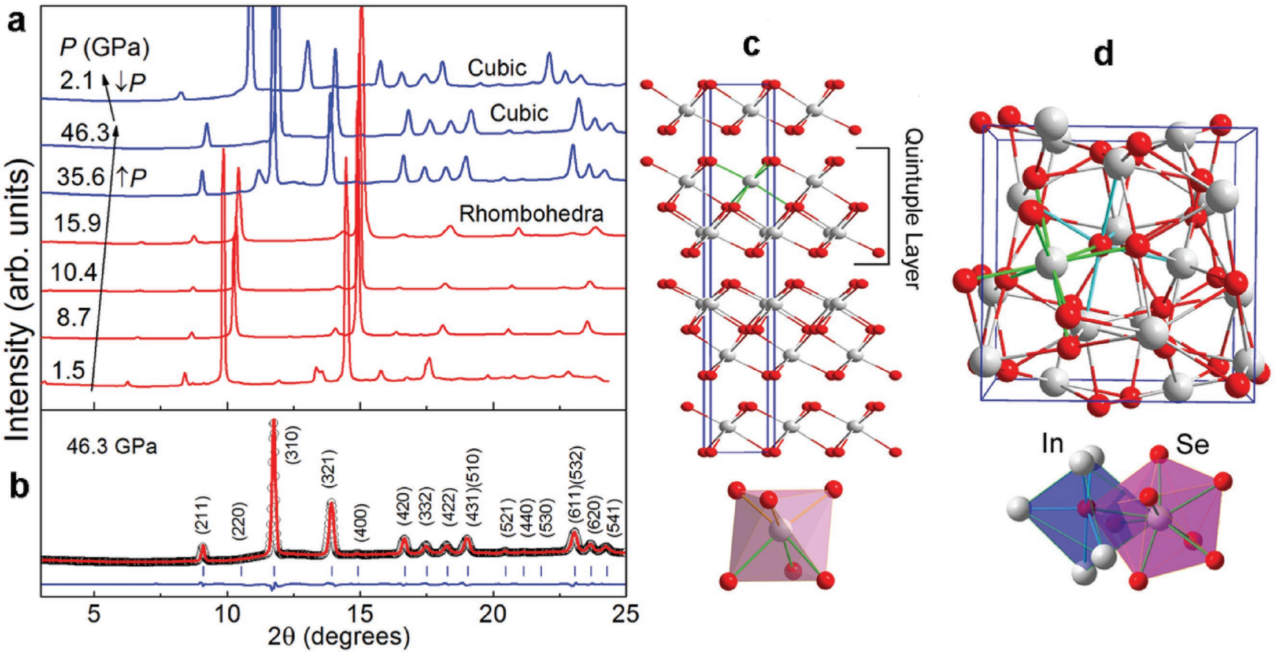

Figure 3. Structural evolution of In_2Se_3 in compression and decompression processes. a) Representative XRD patterns of In_2Se_3 ($\lambda = 0.4959$ Å), and the rhombohedral-cubic structural transition. b) Rietveld refinement of the high-pressure superconducting phase at 46.3 GPa, in which the experimental (symbols) and fitted (red line) patterns are plotted, together. The refining parameters are $R_p = 1.33\%$, $R_{wp} = 1.96\%$. c,d) The low- and high-pressure structures of In_2Se_3.

of 8.2 K. Below 10.7 GPa, the carrier concentration drops sharply with decreasing pressure, which gives rise to weaker electron–phonon coupling, and consequently the loss of superconductivity.

Phonon-softening-induced promotion of superconductivity in compressed CaC_6 was previously reported,[38] in which phonon-softening was caused by the structural instability and heavy strain effect before the structural transition under compression. The scenario is different in the case of In_2Se_3. The structure of high-pressure superconducting phase remains stable during decompression. Furthermore, the superconductivity enhancement in decompressed In_2Se_3 repeats in consecutive compression–decompression cycles. Because of the plastic deformation, usually, the strain effects are different in cyclic compression. Therefore, the strain effect in In_2Se_3, if occurred as CaC_6, should not account for the decompression-driven superconductivity enhancement. Instead, phonon softening is the dominated contributor. Decompression has natural advantage to drive phonon softening, and consequently should be an effective approach to promote T_c of superconductors.

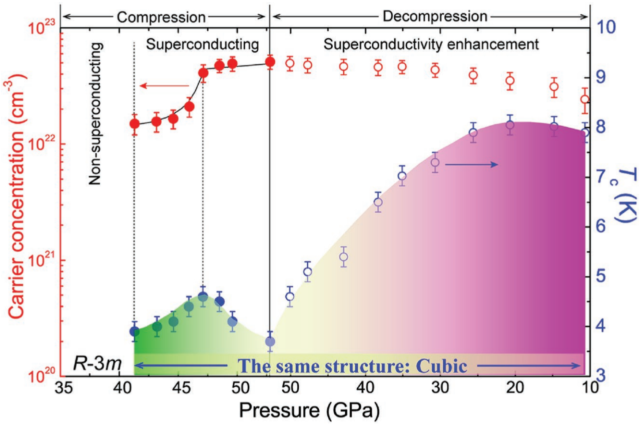

Figure 4. The carrier concentration of In_2Se_3 in pressure cycles. The closed and open symbols represent the compression and decompression data, respectively.

In summary, superconductivity enhancement was observed in pressure quenching. Although the T_c of In_2Se_3 is not high, our observation of decompression-induced superconductivity enhancement encourages the possibility of preserving pressure-induced superconductivity at lower or even ambient pressures with higher T_c. Similar low-dimensional layered materials which can keep the relative higher carrier concentration for electron–phonon coupling at lower decompression pressure, may also demonstrate significant decompression-induced superconductivity enhancement. If the superconductivity quenchable pressure is sufficiently low, around a few GPa, some other approaches such as introducing chemical pressure may undertake the last-mile work of maintaining high-pressure superconductivity in a practical condition, making possible the real application of pressure-induced superconductors.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

layered materials, phonon-modulated superconductivity, pressure, structural transition, superconductivity enhancement

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