Direct Observation of Phonon Avoided-Crossing as the Origin of Ultralow Thermal Conductivity in β-Zn_4Sb_3

Momentum-resolved neutron spectra clearly reveal strong coupling between the acoustic phonon and the rattling mode, resulting in suppressed lattice thermal conductivity.

Thermoelectric (TE) materials are notable for directly converting waste heat into electricity without moving parts or chemical reactions.[1] The efficiency of a TE material is characterized by the dimensionless figure of merit, $zT = S^2\sigma\kappa^{-1}T$, where S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity. A higher zT indicates better conversion performance. Therefore, improving thermoelectric efficiency fundamentally requires increasing S and σ and/or reducing κ.

Among thermoelectric materials, zinc antimonides are the earliest and only Te-free compounds successfully used in thermoelectric generator development.[2] Within this family, p-type β-Zn_4Sb_3 has attracted particular attention due to its intrinsically high zT, achievable even without intentional alloying. β-Zn_4Sb_3 crystallizes in a rhombohedral structure (space group $R\bar{3}c$) and is widely recognized as a phonon-glass electron-crystal material.[3] Structural studies indicate extensive atomic disorder, with excess Zn atoms distributed across multiple interstitial sites. These highly mobile Zn interstitials, which can rapidly hop between available voids as predicted theoretically, are believed to be responsible for the remarkably low lattice thermal conductivity (κ_L) observed in β-Zn_4Sb_3.[4] Combined with a small bandgap (~0.8 eV) that allows for conductivity enhancement through dilute doping, β-Zn_4Sb_3 offers a tunable phonon–electron landscape for efficient TE energy conversion.

Chi-Hung Lee (Tunghai University), Hsin-Jay Wu (National Taiwan University), and their co-workers recently reported the first experimental observation of phonon avoided crossing in β-Zn_4Sb_3 using single-crystal inelastic neutron scattering at **SIKA**, establishing the microscopic origin of its glass-like lattice thermal conductivity (κ_l).[5] Structurally, Zn atoms occupy multiple defect and interstitial sites, producing strong dynamic disorder, while Sb forms a stable rhombohedral framework, with rattling Sb_2 units generating a flat phonon mode. Previous theoretical work proposed that rattlers may hybridize with acoustic phonons to form avoided crossings, a key mechanism underlying ultralow lattice thermal conductivity in host-guest materials such as skutterudites and clathrates. However, direct experimental evidence remains rare, as only single-crystal inelastic neutron scattering can resolve directional phonon dispersions.

The inelastic neutron scattering measurements on single-crystalline β-Zn_4Sb_3 unambiguously resolve a phonon avoided-crossing interaction as the central dynamical feature of this material. As shown in **Fig. 1(a)**, the longitudinal acoustic (LA) branch disperses linearly from Γ, as expected for a crystalline solid at small q, but its behavior deviates markedly near 6–8 meV. Instead of intersecting the low-lying rattling mode, the LA mode gradually flattens. This is a clear indication that its propagation is disrupted

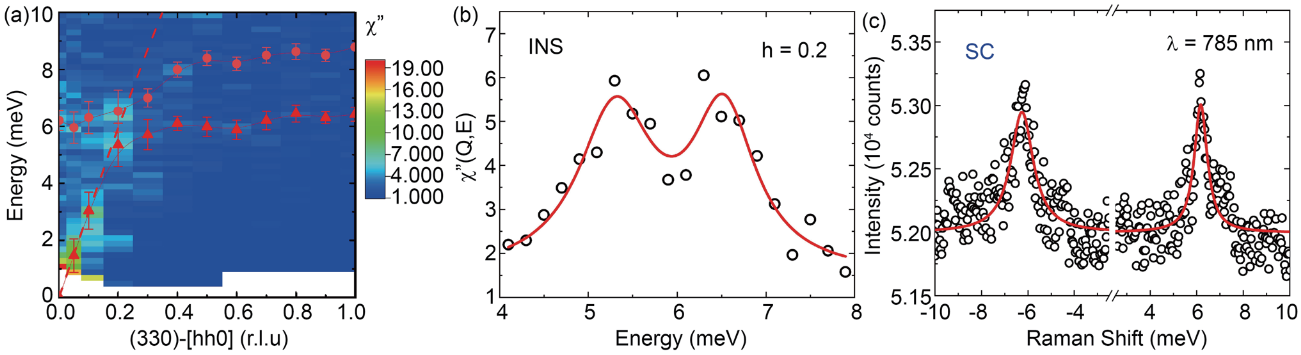

Fig. 1: (a) Longitudinal phonon dispersion of β-Zn_4Sb_3 at 300 K along [hh0]. The dashed line represents a sinusoidal function, and the color scale denotes the dynamic response according to the scattering intensities. Error bars correspond to the full width at half maximum extracted from Lorentzian peak fitting. (b) Constant-Q scan at (330) – [0.2 0.2 0], taken near the acoustic–rattling interaction region, revealing two well-resolved phonon peaks. (c) Room-temperature Raman spectrum of the single crystal excited with a 785 nm laser, confirming the low-lying rattling mode. Solid curves in (a) and (c) represent Lorentzian fits. [Reproduced from Ref. 5]

by another phonon mode. Meanwhile, the rattling mode does not pass through the LA mode but curves upward, deflected away rather than intersecting, resulting in a well-defined energy gap between the two branches. This mutual repulsion of phonon branches constitutes the avoided-crossing event.

The coupling becomes directly visible in the momentum-resolved neutron intensity. In the constant-Q cuts (**Fig. 1(b)**), instead of a single peak, two clear distinct peaks appear simultaneously at the same momentum transfer; this indicates the presence of two phonon branches in close energy proximity. These peaks remain well-separated rather than merging, showing that the modes do not cross but coexist as two resolvable excitations. The existence of this rattling mode is further verified by Raman spectroscopy, where distinct Stokes and anti-Stokes signals appear at 6.17(2) and −6.26(3) meV at room temperature (**Fig. 1(c)**). These symmetric peaks correspond to a rattling mode of ~6.2 meV (≈50 cm^{-1}) at Γ, confirming the presence of a low-lying mode which participates in the avoided crossing observed in neutron scattering.

Overall, the neutron spectra reveal that acoustic phonons in β-Zn_4Sb_3 are intercepted by a low-energy rattling mode and forced into an avoided-crossing state. Because acoustic branches are the primary heat carriers, their dispersion flattening leads to a pronounced reduction in group velocity, thus directly suppressing heat transport. Simultaneously, hybridization with the rattling mode strengthens anharmonic scattering and accelerates phonon decay. The observed linewidth yields an exceptionally short acoustic phonon lifetime of ~0.86 ps, markedly lower than that of conventional crystalline thermoelectrics, and also restricts lattice thermal transport. The reduction of phonon velocity and the ultrafast decay resulting from avoided crossing provides a microscopic mechanism for the intrinsically ultralow κ_L in β-Zn_4Sb_3. (Reported by Chi-Hung Lee, Tunghai University)

This report features the work of Chi-Hung Lee, Hsin-Jay Wu and their co-workers published in Adv. Sci. ***12****, 2411498 (2025).*

ANSTO SIKA – Cold Neutron Triple-Axis Spectrometer
- Inelastic Neutron Scattering
- Materials Science, Condensed-matter Physics

References
1. G. S. Nolas, D. T. Morelli, T. M. Tritt, Annu. Rev. Mater. Res. **29**, 89 (1999).
2. T. Caillat, J. P. Fleurial, A. Borshchevsky, J. Phys. Chem. Solids **58**, 1119 (1997).
3. G. J. Snyder, M. Christensen, E. Nishibori, T. Caillat, B. B. Iversen, Nat. Mater. **3**, 458 (2004).
4. T. Zou, X. Qin, Y. Zhang, X. Li, Z. Zeng, D. Li, J. Zhang, H. Xin,W. Xie, A. Weidenkaff, Sci. Rep. **5**, 17803 (2015).
5. I-L. Jen, C.-Y. Lin, K.-K. Wang, C.-M. Wu, C.-H. Lee, H.-J. Wu, Adv. Sci. **12**, 2411498 (2025).

From Motionless to Mad Dance: Neutron Scattering Reveals the Hidden Driver of the Anomalous Hall Effect

Collinear spins with no static chirality still produce a giant anomalous Hall effect—driven purely by wild quantum spin fluctuations, revealed by neutron scattering. A revolutionary new mechanism for future spintronics.

In today's rapidly advancing technological landscape, the materials within our electronic devices are becoming as critical as the devices themselves. As we pursue faster computing, more efficient communication, and highly secure data storage, researchers are increasingly turning to quantum materials—systems in which electrons behave in unexpected ways. Leading this research is Pengcheng Dai's (Rice University, USA) team, whose studies continue to uncover new magnetic and electronic phenomena in complex materials. Their latest investigation of the kagome-lattice magnet $YbFe_6Ge_6$, shown in **Fig. 1**, marks another significant advance, revealing how subtle quantum effects could one day transform the technologies that shape our lives.

Future electronics aim to control not only electric charge but also electron spin, a field known as spintronics, which promises faster, more efficient, and robust devices. A key phenomenon is the anomalous Hall effect (AHE), where a transverse voltage appears without an external magnetic field.[1]