

# Low-temperature Enhancement of Quantum Hybridization-induced Negative Differential Resistance in a Pb-free 1D Halide Perovskite

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**Abstract**— Low-temperature operation can fundamentally alter quantum transport in low-dimensional materials by suppressing thermal broadening and stabilizing coherent electronic states and ballistic transport. Here, we investigate the temperature dependence of quantum-hybridization negative differential resistance (QHNDR) in a Pb-free one-dimensional halide perovskite using density functional theory combined with nonequilibrium Green's function formalism. We show that QHNDR originates from hybridization between left and right electrode states, forming a delocalized transport channel at low bias that is abruptly disrupted at higher bias. At elevated temperatures, thermal broadening weakens this hybridization, leading to a smeared transport response. In contrast, lowering the electron temperature suppresses thermal broadening and preserves the hybridized transport channel over a wider bias range, resulting in a markedly sharper current peak and a collapse at a higher bias voltage. As a result, the peak-to-valley ratio at 30 K increases by an order of magnitude compared with room temperature. These results indicate that low temperature is not merely a tuning parameter but a key enabler of QHNDR, providing a route to high-performance NDR devices based on low-dimensional perovskites.

**Keywords**—first-principles, quantum hybridization, negative differential resistance, halide perovskite, low temperature

## I. INTRODUCTION

Halide perovskites have emerged as promising materials for electronic and optoelectronic applications, including solar cells, lasers, photodetectors, and light-emitting diodes, owing to their strong light absorption, long carrier diffusion lengths, and excellent photoluminescence [1-3]. Their compositional and structural tunability further enables broad control over electronic properties, making them attractive for diverse device applications. However, their practical deployment remains limited by poor stability. In this regard, low-dimensional halide perovskites have received growing attention because they generally exhibit lower defect densities, improved crystallinity, and enhanced structural stability than their three-dimensional counterparts [4, 5]. These advantages make them attractive not only for optoelectronic technologies but also for emerging nanoelectronic and quantum transport devices.

Low-dimensional halide perovskites have recently been considered as active components of quantum tunneling devices, where transport is governed by the interplay between quantum confinement and interfacial electronic coupling. In particular, halide perovskite-based devices have been proposed as candidates for multi-valued logic [6, 7]. In our previous work, we predicted a pronounced negative differential resistance (NDR) effect with a high peak-to-valley ratio (PVR) in tunneling devices based on trimethylsulfonium germanium triiodide,  $(\text{CH}_3)_3\text{SGeI}_3$  ( $\text{TMSGeI}_3$ ), even under applied strain. In conventional devices, NDR is commonly produced either by band-to-band tunneling in an Esaki diode or by energy-selective tunneling through a double-barrier resonant-tunneling structure [8, 9]. However, we showed that this behavior originates from bias-dependent quantum-mechanical hybridization of electrode states across the  $\text{TMSGeI}_3$  channel. The hybridization is sustained at low bias but collapses abruptly at higher bias, giving rise to quantum-hybridization NDR (QHNDR) [6, 7, 10]. This raises the question of how electronic temperature affects the current contrast associated with the bias-dependent retention and disruption of the quantum-hybridized states.

The previous Pb-based QHNDR study noted that NDR remained robust toward the zero-temperature limit [6], but a systematic temperature dependent analysis of the Pb-free Ge-based junction has not been established. In this work, we investigate the low temperature enhancement of QHNDR in a  $\text{TMSGeI}_3$ -based tunneling device using density functional theory combined with nonequilibrium Green's function calculations. We focus on transport with low (30 K) and room-temperature (300 K) to clarify the effect of suppressed thermal broadening in a device consisting of a semiconducting  $\text{TMSGeI}_3$  channel and semimetallic  $\text{GeI}_3$  electrodes. We find that the PVR at low temperature is enhanced by about a factor of seven compared with that at room temperature. Our nonequilibrium electronic-structure analysis shows that this enhancement originates from the more robust retention of hybridization between electrode states, demonstrating that temperature provides an effective means to control QHNDR in halide perovskite quantum tunneling devices.

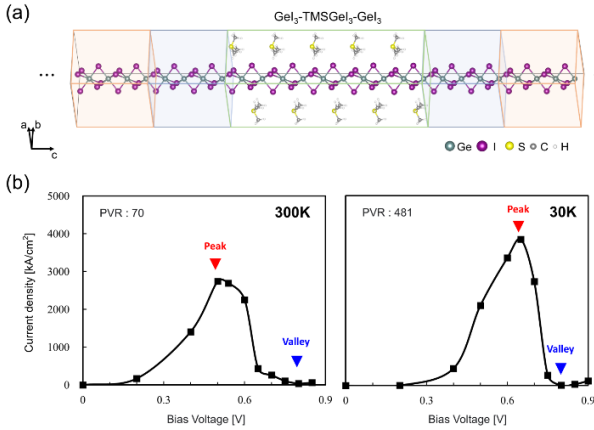


Fig. 1. (a) Structure of non-Pb halide perovskite (TMSGel<sub>3</sub>) electronic device with semimetallic GeI<sub>3</sub>. (b) Comparison of the temperature-dependent I-V curves at room temperature (300 K) and low (30 K), where the red and blue triangles indicate the peak and valley points, respectively.

## II. METHOD

All equilibrium density functional theory (DFT) and the non-equilibrium Green's function (NEGF) calculations [11] were performed using the SIESTA software package [12]. We adopted Perdew-Burke-Ernzerhof parameterization of generalized gradient approximation for solids (PBEsol) [13], double  $\zeta$ -plus-polarization-level numerical atomic orbital basis sets, and the Troullier-Martins type norm-conserving pseudopotentials [14]. The mesh cutoff of 200 Ry for the real-space integration was used. Geometry optimizations were performed until the total residual forces on each atom were below 0.02 eV/Å. The k-point meshes were  $4 \times 4 \times 10$  Monkhorst-Pack grid. The surface Green's functions  $g_s$  were obtained from DFT calculations. After nonequilibrium calculations, the matrix Green's function formalism was used for the electron transmission calculations according to

$$T(E; V_b) = \text{Tr}[\Gamma_L(E; V_b)G(E; V_b)\Gamma_R(E; V_b)G^\dagger(E; V_b)] \quad (1)$$
 Where  $G$  is the retarded Green's function for the channel region and  $\Gamma_{L/R}$  are the broadening matrices. The current density was calculated using the Landauer-Büttiker formula,

$$J(V_b) = \frac{2e}{hA} \int_{\mu_L}^{\mu_R} T(E; V_b) [f(E - \mu_R) - f(E - \mu_L)] dE \quad (2)$$

Transmission eigenchannels were evaluated using the Inelastica code [15].

## III. RESULT AND DISCUSSION

Using semimetallic GeI<sub>3</sub> as the electrodes and semiconducting TMSGel<sub>3</sub> as the channel, we constructed a GeI<sub>3</sub>-TMSGel<sub>3</sub>-GeI<sub>3</sub> junction to investigate the temperature dependence of the NDR behavior (Fig. 1a). The J-V characteristics show that the NDR response is strongly affected by temperature (Fig. 1b). As the electronic temperature decreases from 300 K to 30 K, the device exhibits an enhancement of the NDR characteristics. The peak voltage shifts to higher bias, while the peak current density increases. As a result, the PVR increases from 70 at 300 K to 481 at 30 K.

To clarify the microscopic origin of the QHNR mechanism, we first analyze the representative 300 K case, where the peak and valley occur at 0.5 and 0.8 V, respectively. The PLDOS of the full device and the PDOS of the channel region were analyzed at 0.0, 0.5, and 0.8 V, corresponding to the equilibrium, peak, and valley conditions, respectively (Fig. 2a). At 0.0 V, the left and right semimetallic electrode states penetrate into the TMSGel<sub>3</sub> and form hybridized states through the channel. As the voltage increases, the hybridized states maintain up to 0.5 V, which leads to the current peak. At 0.8 V, however, the junction-spanning hybridization collapses, strongly suppressing the transmission channel, and the NDR valley appears.

The channel PLDOS makes this evolution more explicit by showing how the initially hybridized state gradually separates into left- and right-localized states as the bias increases. It also shows that the transport window is dominated mainly by Ge, I-derived states, indicating that charge transport is governed primarily by the inorganic Ge-I framework of the TMSGel<sub>3</sub> rather than by the organic TMS ligand. This bias-dependent evolution of the hybridized state is summarized schematically in Fig. 2b.

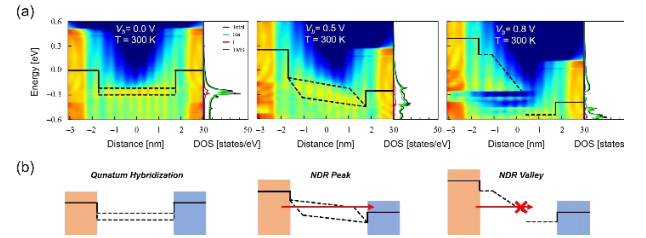


Fig. 2. (a) PLDOS of the full device and PDOS of the channel region at 300 K under  $V_b = 0.0, 0.5$ , and  $0.8$  V. In the channel PDOS, black, green, red, and blue lines indicate the total, Ge-, I-, and TMS-derived contributions, respectively. (b) Schematics of the QHNR mechanism

We next examine how temperature affects the bias-dependent evolution of the states responsible for the QHNR mechanism by comparing the PLDOS and transmission spectra obtained at the peak and valley biases for 300 K and 30 K (Fig. 3). At both temperatures, the PLDOS at peak bias exhibits a continuous distribution of spectral weight across the GeI<sub>3</sub>-TMSGel<sub>3</sub>-GeI<sub>3</sub> junction, consistent with the presence of a hybridized transport state extending across the junction. The corresponding peak bias shifts from 0.5 V at 300 K to 0.65 V at 30 K. Despite this higher peak bias at lower temperature, the spectral weight remains spatially connected across the junction, indicating that the hybridized transport pathway is preserved at the peak bias. In addition, the dominant transmission resonance within the bias window becomes sharper and reaches a higher maximum value at 30 K than at 300 K, consistent with reduced thermal broadening at lower electronic temperature.

At the common valley bias of 0.8 V, however, the PLDOS and transmission spectra remain qualitatively similar at 300 K and 30 K. The continuous spectral pathway is disrupted at both temperatures. The states resolved in the PLDOS are localized predominantly near the left and right electrodes, while the transmission within the bias window is strongly suppressed. These features are consistent with the breakdown of junction-spanning quantum-hybridized transport states. Thus, decreasing

the electronic temperature shifts the hybridized peak state to higher bias, reduces the broadening of the peak transmission resonance, and enhances the peak-to-valley current density contrast. Consequently, the combined effects of the enhanced peak current density and the suppressed valley current density increase the PVR from 70 at 300 K to 481 at 30 K.

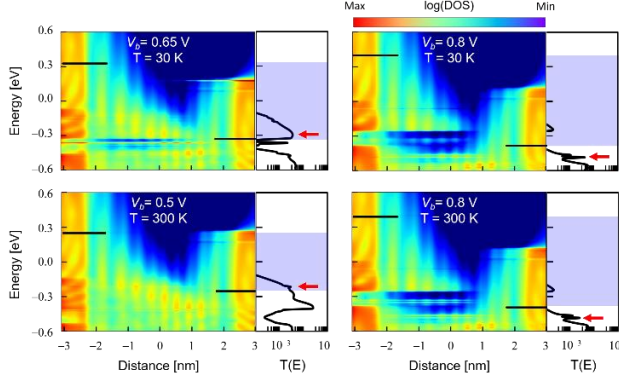


Fig. 3. Comparison of the PLDOS and transmission spectra at the peak and valley bias voltages at 30 K and 300 K. The shaded region denotes the bias windows, and the red arrows indicate the dominant transmission peaks that significantly contribute to the current density

To verify whether the transmission features correspond to spatially connected current-carrying states, we analyzed the transmission eigenchannels (Fig. 4). The eigenchannel energies were chosen from the transmission maximum indicated by red arrows in Fig. 3. At the NDR peak, the eigenchannels exhibit appreciable eigenchannel amplitude extending from the GeI<sub>3</sub> electrode into the TMSGeI<sub>3</sub> channel at both temperatures. Importantly, such channel-side extension is retained even when the peak bias shifts from 0.5 V at 300 K to 0.65 V at 30 K. This indicates that the high-transmission hybridized states remain effective at higher peak bias as the electronic temperature decreases.

At the common valley bias of 0.8 V, the eigenchannel distributions are qualitatively different from those at the peak. Although finite amplitude is still visible near the electrode, it decays rapidly inside the TMSGeI<sub>3</sub> channel and does not form a continuous pathway across the junction. Therefore, the partial electrode-side penetration observed at the valley should not be interpreted as the recovery of an effective transport channel. Instead, the valley state remains characterized by the loss of junction-spanning connectivity, consistent with the strongly suppressed transmission and low valley current density.

These eigenchannel results support the PLDOS and transmission analysis. The low temperature enhancement of QHNDR is not simply due to a spatial expansion of eigenchannels. Rather, it reflects the increased contrast between spatially hybridized high transmission states at the NDR peak and collapsed states at the NDR valley.

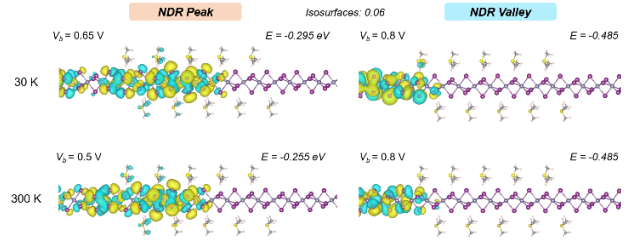


Fig. 4. Eigenchannel distributions corresponding to the energies marked by the red arrows in Fig. 3. The isosurface level is  $6 \times 10^{-2}$ .

Therefore, temperature dependence can be understood mainly as an enhancement of the current contrast between the peak and valley regimes. At lower electronic temperature, the sharper electrode occupation functions suppress thermally smeared contributions to the valley current, leading to a larger PVR.

#### IV. CONCLUSION

To summarize, using first-principles DFT-NEGF calculations, we investigated the temperature-dependent QHNDR behavior of a Pb-free one-dimensional GeI<sub>3</sub>-TMSGeI<sub>3</sub>-GeI<sub>3</sub> junction. Analyses of the PLDOS, transmission spectra, and eigenchannels revealed that the NDR originates from the bias-induced formation and breakdown of a junction-spanning hybridized transport state. At the peak bias, the hybridized state forms a continuous transport pathway dominated mainly by Ge, I-derived states, whereas at the valley bias, it separates into left- and right-localized states, strongly suppressing transmission. As the electronic temperature decreases, the hybridized peak state persists to higher bias, while reduced thermal broadening produces a sharper and higher transmission resonance. In contrast, the transport pathway remains spatially interrupted at the valley bias. Consequently, the enhanced peak current density and suppressed valley current density increase the PVR from 70 at 300 K to 481 at 30 K. These findings clarify the microscopic origin of temperature-enhanced QHNDR and highlight Pb-free one-dimensional halide perovskites as promising candidates for low-temperature NDR devices.

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