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Supplementary Material

Switching of dominant magnetic exchange interaction between tetrahedral-octahedral and octahedral-octahedral sites in $(Mn_{1-x}Cr_x)_3O_4$ spinels

G. D. Dwivedi,[a] Tsung-Wen Yen,[a] S. M. Kumawat,[ab] C. W. Wang,[c] D. Chandrasekhar Kakarla,[a] A. Tiwari,[a] H. D. Yang,[a] S. M. Huang,[a] C. M. Chung,[a] S. J. Sun,[da] H. Chou[*ad]

[a]*Department of Physics, and Center of Crystal Research, National Sun Yat-sen University, Kaohsiung, 80424, Taiwan, R.O.C.*

[b]*International Ph.D. program for Science (IPPS), National Sun Yat-sen University, Kaohsiung, 80424, Taiwan, R.O.C.*

[c]*National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan, R. O. C.*

[d]*Department of Applied Physics, National University of Kaohsiung, Kaohsiung, Taiwan, R. O. C.*

[*]Corresponding authors: hchou@mail.nsysu.edu.tw (H. Chou)

Wannierization:

The numerical approach to fit the exchange parameters is discussed here. First, to circumvent the difficulties of calculating the green function using plane-wave basis sets, one needs to convert the DFT plane wave results into maximally-localized Wannier functions (MLWFs).[1-3] The MLWFs are functions spreading locally in the vicinity of Wannier centers, of which the exact spatial locations are *a priori* unknown, and need to be determined self-consistently. Common approaches to determine MLWFs include minimizing the value of Ω, which is a function that measures the spread of the Wannier functions. After the minimization procedure satisfied the required criteria, one stops the minimization procedure and arrives at the finalized MLWFs. If the quality of MLWFs is well enough, the calculated properties such as electronic properties, transport properties, or magnetic exchange coupling parameters using the MLWFs are expected to be similar to those calculated from *ab initio* methods. Visually, the side-by-side comparison of the band structure of *ab initio* calculation, and the band structure of MLWFs can be used as a quick way to evaluate the quality of MLWFs is good or bad. If the two band structures are indiscernible, then we have confidence that MLWFs are successful, and that their subsequent calculated properties

are reliable for analysis and discussions. This part of the numerical procedure was carried out using the Wannier90 code. The Wannierization quality can be evaluated in Fig. S1. One can see that the DFT band structure in Fig. S1(a) and the one interpolated by the Wannier function (Fig. S1(b)) bear close resemblance, in terms of exact band energies, and also their band dispersive patterns at all *K* points. To provide clearer view we have merged both graphs in to one and enlarged at the vicinity of Fermi-level (Fig. S2). This indicates that the Wannierization is successful for our system, and thereby the subsequent calculation of Green functions, and exchange parameters are reliable for the discussion.

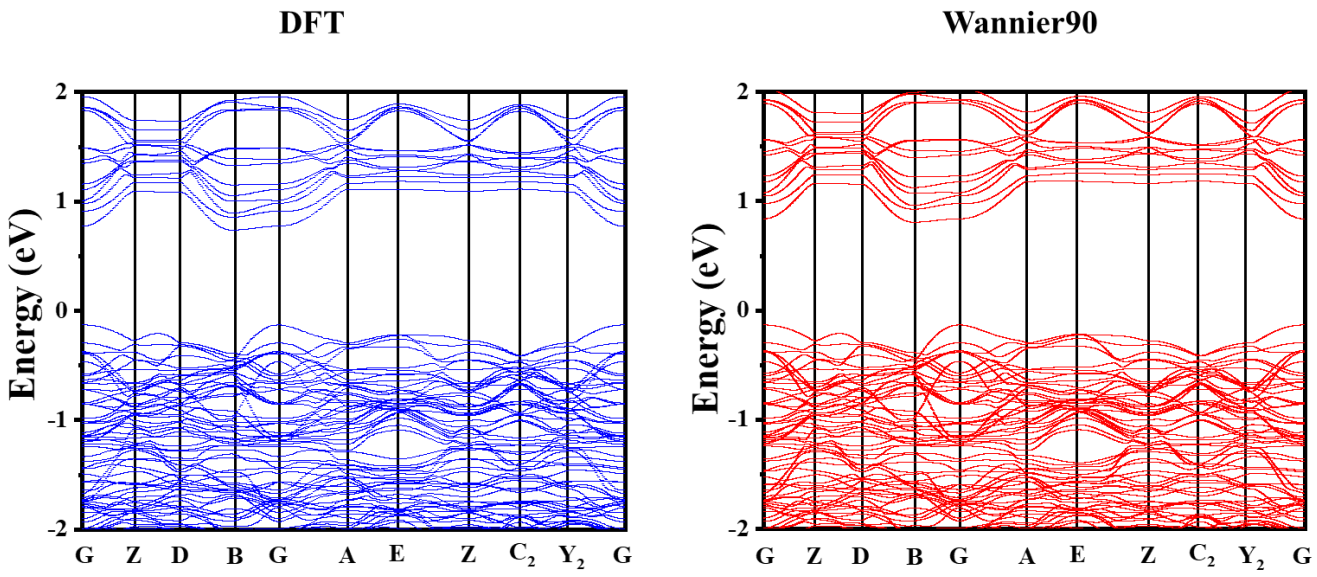

Fig. S1: (a) The band structure of $Mn_{2.7}Cr_{0.3}O_4$ from DFT calculations (blue lines), and (b) Wannier function-interpolated band structure (red lines) are compared. The results for both are almost identical, implying the quality of Wannierization is acceptable. The bands beyond 5 eV are not included in the Wannierization procedure.

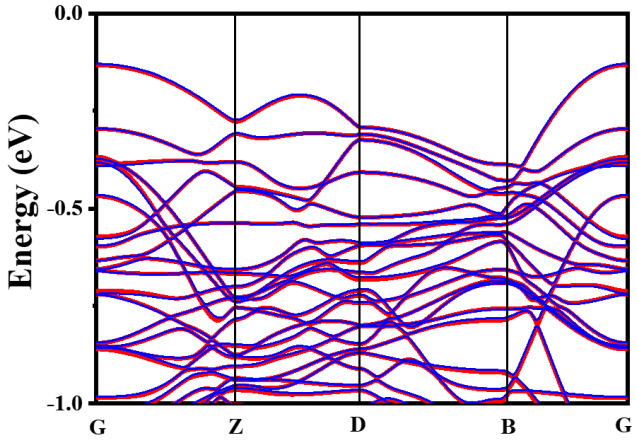

Fig. S2: DFT calculations (blue lines) and Wannier function (red lines) are merged and enlarged at the vicinity of Fermi-level to verify the quality of Wannierization. This verifies that the quality of Wannierization is acceptable.

Frequency-dependent dielectric property:

To check the role of Maxwell-Wagner polarization in the observed dielectric peak around T_N, we have measured the temperature-dependent dielectric constant at various frequencies. It is clearly evident that the dielectric peaks around T_N are independent of frequencies. This result confirmed that Maxwell-Wagner polarization does not contribute to the dielectric peak around T_N and the peak appears due to magneto-dielectric coupling.

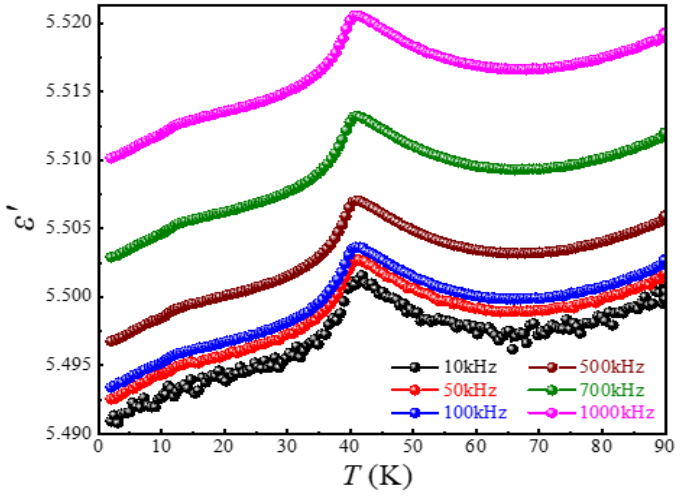

Fig. S3. Temperature-dependent dielectric constant for $Mn_{2.7}Cr_{0.3}O_4$ at various frequencies are shown. Dielectric curves of 500 kHz, 700 kHz, and 1000 kHz are adjusted for clear comparison.

References:

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2 G. H. Wannier, Rev. Mod. Phys., 1962, **34**, 645.

3 N. Marzari and D. Vanderbilt, Phys. Rev. B, 1997, **56**, 12847.