Infrared evidence of a Slater metal-insulator transition in NaOsO₃

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The magnetically driven metal-insulator transition (MIT) was predicted by Slater in the fifties. Here a long-range antiferromagnetic (AF) order can open up a gap at the Brillouin electronic band boundary regardless of the Coulomb repulsion magnitude. However, while many low-dimensional organic conductors display evidence for an AF driven MIT, in three-dimensional (3D) systems the Slater MIT still remains elusive. We employ terahertz and infrared spectroscopy to investigate the MIT in the NaOsO₃ 3D antiferromagnet. From the optical conductivity analysis we find evidence for a continuous opening of the energy gap, whose temperature dependence can be well described in terms of a second order phase transition. The comparison between the experimental Drude spectral weight and the one calculated through Local Density Approximation (LDA) shows that electronic correlations play a limited role in the MIT. All the experimental evidence demonstrates that NaOsO₃ is the first known 3D Slater insulator.

In the last sixty years considerable effort has been devoted to the study of the MIT in transition metal oxides. In their fundamental papers Mott and Hubbard proposed that the electron-electron interaction (U) is the key ingredient of the MIT. Electronic correlations may strongly renormalize the kinetic energy (t) of charge-carriers leading to the formation of a gap at the Fermi energy and then to an insulating state regardless of magnetic correlations. Temperature and/or pressure may increase the t/U ratio, thus inducing a transition (Mott-Hubbard transition) from the insulating to the metallic state. V₂O₅, Ni(S,Se)₂ and NdNiO₃ are considered textbook examples of Mott-Hubbard materials. On the other hand, Slater suggested a different mechanism for the MIT: he stated that antiferromagnetic order alone could open up a gap. The establishment of a commensurate AF order induces an opposite potential on each nearest electron site which doubles the magnetic unit cell and cuts the first Brillouin zone. This results in a splitting of the occupied bands and, in case of half-filling, in a gap for charge excitations. So far the only evidence of magnetically driven MITs was found on low dimensional organic compounds as Bechgaard salts, while the 3D candidates Cd₅O₇O₂, Ln₄Ir₂O₇ could not be classified as Slater insulators due to magnetic frustration in their pyrochlore lattice. Experimental indications of a Slater transition have never come up until last year. By using neutron and x-ray scattering, Calder et al. have shown that in the perovskite NaOsO₃ the MIT at T_{MIT} = 410 K, previously discovered on the basis of transport and magnetic measurements, is concomitant with the onset of long-range commensurate three-dimensional antiferromagnetic order. As a perovskite with octahedral environment Os⁷⁺O₆, NaOsO₃ shows a half-filled 5d⁸ electronic configuration. In addition, 5d orbitals are far more spatially extended than those in 3d systems, thus electron-electron interactions is expected to play a minor role in this compound, as also recently argued from theoretical calculations. In this work we probe the low-energy electrodynamics of NaOsO₃ across the MIT by terahertz and infrared spectroscopy. From an analysis of the optical spectral weight we establish that NaOsO₃ is a weakly correlated material. We also show that, at variance with a Mott-Hubbard MIT, the optical conductivity does not vanish at T_{MIT} as the charge gap opens up in a continuous way in agreement with the second order character of the MIT. Those experimental results definitively clarify the nature of the three-dimensional MIT in NaOsO₃ in terms of the Slater mechanism.
Results

The reflectance $R(\omega)$ of NaOsO$_3$ is shown in Fig. 1 in the 0–1000 cm$^{-1}$ frequency range. At 450 K it shows a metallic response, approaching unity at zero frequency. After crossing $T_{\text{MIT}}$, this metallic behavior depletes progressively and, in the antiferromagnetic insulating phase, two complex phononic structures start to appear as a consequence of the reduced screening. At 5 K there is a well visible double phonon peak with characteristic frequencies around 300 cm$^{-1}$ and 330 cm$^{-1}$ and another phonon resonance at 650 cm$^{-1}$. Moreover, $R(\omega)$ shows a rising tail for $\omega \to 0$ related to a low-frequency mode centered around 20 cm$^{-1}$ (see discussion below). In the inset of Fig. 1 we show instead the reflectance over the entire measured range in the metallic (450 K) and in the insulating state (5 K). It is well evident that the MIT determines a strong modification of the electronic properties of NaOsO$_3$ over a frequency scale up to nearly 10000 cm$^{-1}$.

The main panel of Fig. 2 shows the optical conductivity $\sigma(\omega)$ on a linear scale in the 0–10000 cm$^{-1}$ frequency range as obtained from reflectance data by Kramers-Kronig relations. The same quantity is represented in the inset on a logarithmic scale for selected temperatures above and below $T_{\text{MIT}}$. The symbols on the vertical axis indicate dc values of the conductivity, calculated from transport measurements. The inset shows the optical conductivity on a log scale at selected temperatures. The Drude-Lorentz fitting results (see text) are indicated by open symbols.

The optical conductivity at 450 K shows a metallic behavior with a broad pseudo plasma-edge around 12000 cm$^{-1}$ which separates the low energy excitations from a huge interband transition around 20000 cm$^{-1}$. This absorption band is mainly associated to charge-transfer excitations among Os 5d and O 2p states. Below $T_{\text{MIT}}$, the metallic conductivity sharply decreases in the far-infrared through a transfer of spectral weight (SW) to a mid-infrared (MIR) band centered around 3000 cm$^{-1}$. The low-frequency SW depletion is nearly exhausted at 200 K where the MIR is located at about 4000 cm$^{-1}$.

A broad feature centered around 22 cm$^{-1}$ can be seen in the insulating phase between 5 and 200 K and it is probably hidden at higher-$T$ by the free carrier background. We associate this peak to an antiferromagnetic resonance. Indeed, the insulating phase of NaOsO$_3$ corresponds to a G-type AF configuration where the spins are oriented along the $c$-axis. The antiferromagnetic mode corresponds to a precession of spins along $c$ induced by some degree of magnetic anisotropy.

The loss of SW in the far-infrared mirrors the opening of an optical gap $E_g$ already distinguishable at 380 K, whose size increases for decreasing $T$. One can then extract $E_g$ from data in Fig. 2 and compare its temperature dependence with that expected for a second order (Slater) phase transition. The optical conductivity in the insulating AF phase can be described through the following equations:

$$\sigma_1(\omega) = m\omega + q \quad \text{for } \omega \leq E_g$$

(1)

and

$$\sigma_1(\omega) = A\left[\omega - E_g(\omega)\right]^2 \quad \text{for } \omega \geq E_g$$

(2)

Here, the linear term describes the low-frequency background which is mainly due to thermal excited charge-carriers across the insulating gap (see below). For higher frequencies instead, we assume a behavior of $\sigma_1(\omega)$ similar to that of a semiconductor in the presence of direct band to band transitions. The curves thus obtained, reported as dashed lines in the inset of Fig. 3, nicely fit the rising edge of $\sigma_1(\omega)$ at all temperatures with $\omega = \frac{1}{2}$. An estimate of the gap $E_g(T)$ is then obtained through the intersection between Eq. 1 and Eq. 2 and its temperature behavior, which is plotted as empty circles in Fig. 3, resembles that of a Bardeen-Cooper-Schrieffer (BCS) function in good agreement with the second order character of the MIT. Let us mention that similar gap values can be also achieved by substituting the linear conductivity (Eq. 1) with a Drude term. Therefore the error bars in Fig. 3 take into account the small variation of $E_g(T)$ in terms of different extracting methods and the smearing effect in the conductivity edge due to the temperature.

A BCS-like analytic expression for $E_g(T)$ can be written as:

$$E_g(T) = \frac{E_g(0)}{\tanh\left[\frac{E_g(T)}{T_{\text{MIT}}}\right]}$$

(3)

This function well describes data in Fig. 3 furnishing a value of $E_g(0) = 825 \pm 25$ cm$^{-1}$ and a $T_{\text{MIT}} = 400 \pm 10$ K in fair agreement with
the value ($T_{\text{MIT}} = 410 \text{ K}$) obtained through transport and magnetic measurements. Moreover, $E_g(0)/k_B T_{\text{MIT}} = 3.0 \pm 0.1$, thus suggesting a weak coupling regime in agreement with a Slater scenario.

As mentioned before, the gap opening corresponds to a loss of SW that is nearly conserved for $\omega_c \simeq 15000 \text{ cm}^{-1}$. This energy scale is well captured by the LDA + U calculation reproducing, for a G-type antiferromagnetic order, the insulting state for a moderate value of $U \sim 1-2 \text{ eV}$.

The SW redistribution can be analyzed in detail by fitting $\sigma_1(\omega)$ through a multi-component Drude-Lorentz (D-L) model. The complex optical conductivity is written in terms of a Drude contribution and five Lorentzian curves as:

$$\sigma_1(\omega) = \sigma_1(\omega_c, T) \frac{1}{1 + \omega_i / \omega_c}$$

and it is proportional to the number of carriers taking part to the optical absorption up to a cutoff frequency $\omega_c$. The SW is nearly conserved for $\omega_c \simeq 15000 \text{ cm}^{-1}$. This energy scale is well captured by the LDA + U calculation reproducing, for a G-type antiferromagnetic order, the insulting state for a moderate value of $U \sim 1-2 \text{ eV}$.

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Optical measurement. We performed near-normal reflectance measurements on an accurately polished sample using a Michelson interferometer in the frequency range from 10 cm\(^{-1}\) (this limit varies for some temperatures) to 15000 cm\(^{-1}\). Tetrahedrons and subterahertzs (\(\omega < 50 \text{ cm}^{-1}\)) measurements were performed using radiation produced at the SISSI\(^{26}\) and IRS\(^{27}\) infrared beamlines at Elettra and Bessy-II synchrotrons respectively. A gold or silver (depending on the spectral range) coating was evaporated \textit{in situ} on the sample surface and used as a reference. The optical conductivity was calculated by Kramers-Kronig transformations. Low-frequency reflectance data were extrapolated with standard methods (Hagen-Rubens or constant lines) taking into account the resistivity dc values measured in samples of the same batch. A high-frequency tail\(^{11}\) was instead merged to the data above 15000 cm\(^{-1}\).

LDA calculation. The \(K_{\text{LDA}}\) was obtained from first-principles calculations within Local Density Approximation (LDA) of density functional theory. The electronic structure was calculated from full-potential augmented plane wave (APW) methods with the WIEN2k package\(^{28}\). The spin-orbit interaction was included within self-consistent calculations. The lattice constants and atomic positions were taken from experimental values\(^{10}\). The Muffin-tin radii were chosen as 2.0, 1.8 and 1.7 a.u. for Na, Os, and O, respectively. The cutoff wave number \(K\) in interstitial region was set to \(K = 8\), where \(R\) is the smallest atomic radius, i.e., 1.7 a.u. for O. The integration over Brillouin zone was performed by a tetrahedron method with up to 1960 k-points in an irreducible zone. The optical conductivity and plasma frequency were estimated from the momentum matrix elements as described in Ref. 29. Since NaOsO\(_3\) has orthorhombic symmetry with \(Pmna\) space group, the optical conductivity tensors are characterized by three diagonal elements \(\sigma_{xx}, \sigma_{yy}\), and \(\sigma_{zz}\). Accordingly, we obtained plasma frequency for each direction as \(\omega_{pzz} = 2.2 \text{ eV}, \omega_{pyy} = 1.8 \text{ eV}, \omega_{pxx} = 2.4 \text{ eV}\). The averaged plasma frequency \(\omega_{p}(\text{LDA}) = \left(\omega_{pxx} + \omega_{pyy} + \omega_{pzz}\right)/3\) was estimated as 2.1 eV.

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Author contributions
Y.S. and K.Y. fabricated and characterized \(\text{NaOsO}_3\) samples. I.L.V., A.P., P.D.P., O.L., and S.L. carried out the terahertz experiments and data analysis. M.A. was responsible of the LDA calculations. S.L. was responsible for the planning and the management of the project with inputs from all the co-authors, especially from I.L.V., A.P. and K.Y. All authors extensively discussed the results and the manuscript that was written by I.L.V., A.P. and S.L.

Additional information
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