Comment on "Indirect L to T point optical transition in bismuth nanowires"

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In the paper by A. J. Levin, M. R. Black, and M. S. Dresselhaus [Phys. Rev. B **79**, 165117 (2009)] absorption features in infrared spectra are attributed to certain electronic transitions in bismuth nanowires. Our Comment refers to the experimental spectra presented in this paper and explains how a better sample characterization would have improved the reliability of the conclusions from infrared spectra.

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In a recent paper[1] Levin *et al.* calculated the energy difference between the L and T point valence-band edges as a function of Bi nanowire diameter and crystalline orientation and compared this result with the absorption features in infrared spectra, which are attributed to this electronic transition. By repeating previously published measurements of three different groups[2–4] on the same experimental setup, the authors claim to have demonstrated that the previously observed differences between the infrared (IR) spectra of Bi nanowires oriented in the $[01\bar{1}2]$ and $[11\bar{2}0]$ directions are physical in nature and were not caused by differences in experimental setup. They therefore conclude that the differences in the optical properties of the nanowires from the different groups are partly the result of the different crystalline orientations of their nanowires. We do not want to comment on the theory presented in Ref. 1. We only have strong concerns regarding the significance of the IR spectra presented in Ref. 1.

In general, IR spectroscopy can be a very sensitive method[5] also for metallic systems.[6–8] Even as ellipsometric method it can reach submonolayer sensitivity.[9] Additionally to the performance of the Fourier-transform IR spectrometer, the sensitivity of the detector, and the intensity of the light source, the stability of the setup (including the concentration of absorbing molecules in the optical beam path) and reliable reference measurements are crucial. Such reference measurements are, for example, the measurement of the bare substrate under identical conditions or the measurement of the pure host material, respectively. Also, the details of the measurement geometry and the polarization of incident light always should be given in a publication since they determine the spectral shape of the measured features.

In detail Fig. 8 of Ref. 1, its caption, the respective text parts, and the given reference[2] do not contain clear information whether the alumina template was removed completely, such as x-ray diffraction (XRD) measurements. The information about the presence of alumina is important for any conclusion since alumina has phonon energies up to about 900 cm^{-1}.[10] In near-normal reflectance, as used in Ref. 1, alumina shows a reststrahl band with a tail to 1000 cm^{-1} that may contribute to the observed change in reflectance.

Figure 9 shows a transmission measurement of a KBr pellet with Bi nanowires. The authors assign the observed spectral features to L-T transitions in the Bi nanowires. We have strong doubts concerning this interpretation as the spectral position and line shape resemble vibrational modes of nitrate impurities in KBr pellets, see Ref. 11. Furthermore, the spectrum is not compared to that of a KBr pellet produced of the same KBr powder without wires. Such comparison would clarify the spectral analysis. It is not sufficient to take the disappearance of the IR signals with annealing as proof that the Bi wires are the origin of the signal as done in Ref. 3 since annealing also removes those impurities.[11]

Figure 10 should show reflectance spectra from Bi wires with two different diameters on a silicon substrate. It is already known from Ref. 4 that a single Bi wire with a diameter of 120 nm gives a signal of about 2% in transmittance when measured with 8 μm aperture. Accordingly, with the 1.5 mm aperture used here, around 40 000 Bi wires would be needed for a similar signal strength. But unfortunately the authors do not give any information on the wire density within the measurement spot. Moreover, since the expected IR feature from Bi nanowires are so small, normalization to the pure substrate spectrum (including various absorption features from substrate wafer and background) is recommended for the observation of Bi wire bands. As the wire density is not given and as the spectrum from an Au mirror with much higher reflectance than the silicon substrate was used as reference, which leaves all background features in the spectrum, we strongly disagree with the author's statement that "our results confirm that the L-T transition peaks visible in $[01\bar{1}2]$-oriented nanowires are absent in $[11\bar{2}0]$-oriented nanowires." In fact, such experimental verification needs further measurements that are sensitive enough to detect possible signals from the Bi wires. Even the qualitative conclusion that the absorption from the sample of Black *et al.* is larger than that from the sample of Cornelius *et al.* cannot be drawn because the signal strength would have to be normalized per wire or cm^3 of Bi.

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