Reply to "Comment on 'Indirect L to T point optical transition in bismuth nanowires' "

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In the preceding Comment, the authors raise several questions regarding the properties of bismuth nanowire samples studied in the experimental section of Phys. Rev. B **79**, 165117 (2009) and the interpretation of the resulting infrared spectra. We address their concerns by discussing each sample in detail and providing additional relevant information.

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I. INTRODUCTION

We appreciate the interest in our paper and welcome an open dialog about our work and the work of those whose papers we referenced. The main goal of the experimental section of our original paper was to demonstrate that the salient spectral features of three bismuth nanowire samples, each made and characterized by a different research group, could be qualitatively reproduced on a single Fourier transform infrared (FTIR) apparatus. Two groups (Black *et al.* and Reppert *et al.*) had measured an intense absorption feature that dominates the IR optical properties of their samples. The sample of a third group (Cornelius *et al.*) did not display this very large optical-absorption feature but instead showed a far weaker one. In the experimental section of Levin *et al.* we confirmed the presence of the large feature in two of the samples and not the third, even though our setup differed from the previous setups in many ways, including some that the authors of the Comment rightly point out as being important for determining the line shape and quantifying the intensity. Thus, we arrived at the conclusion that the large differences in measurement setups between the various groups did not lead to the large difference in the resulting optical measurements but instead that the different samples that were measured indeed have different optical properties.

The authors of the Comment raise some questions regarding our experimental setup and request more details on reference measurements of the measured samples. In order to allay their concerns and provide additional relevant information, we would like to discuss each set of samples in greater depth.

II. BLACK *et al.* SAMPLES

In their original experiment,[1] Black *et al.* measured their bismuth nanowire samples in the reflectance mode against a gold background and we therefore did the same for the measurements in our paper.[2] The authors of the Comment express concern that some of the absorption features in the measured spectra of these samples may be attributable to alumina instead of Bi nanowires. We note that in previously published work, the IR spectra from the same alumina template is compared to IR spectra from bismuth nanowire samples in alumina and although there is a small feature in the IR spectrum of the bare alumina, the absorption from this feature is significantly weaker than that from the bismuth nanowires.[3]

In addition to optical data indicating that all the alumina was etched away, there have been many other characterization methods which indicate that a wet etch completely removes the alumina template from a bismuth nanowire sample. For example, Cronin *et al.* report transmission electron microscopy images of such free-standing bismuth nanowires and they have investigated the bismuth oxide formed on the nanowires after the alumina has been removed.[4]

Another line of evidence indicating that the measured spectra of these samples indeed stem from Bi nanowires and not from the template can be seen in Fig. 10(a) of Ref. 1 (reproduced below as Fig. 1), which compares the reflectance from four bismuth nanowire samples inside an alumina template, each with a different level of *n*-type doping. As the bismuth nanowires experience more heavy *n*-type doping, the Fermi energy rises and the T point carrier pocket fills with electrons. At a certain doping level, electrons excited
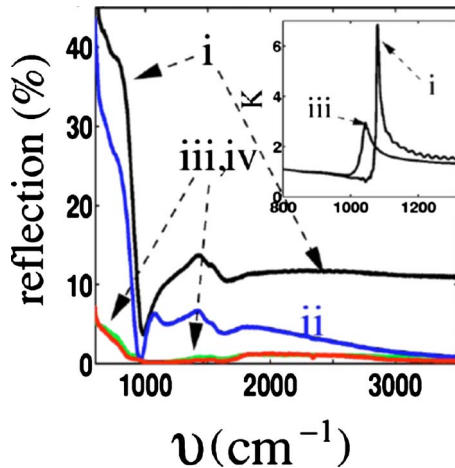
FIG. 1. (Color online) The measured wave-number dependence of the reflection of (i). undoped, (ii) lightly *n*-type doped, (iii) medium *n*-type doped, and (iv) heavily *n*-type doped bismuth nanowires. The inset shows the calculated wave number dependent *K*, the imaginary part of the index of refraction of the iii. medium doped and i. undoped samples (Ref. 1).

from the L point valence band no longer have empty states in the T point carrier pocket to occupy, and the optical absorption from the L to T point electronic transition is then quenched. Hence, the L-T point transition dominates the spectra labeled (i) and (ii) in Fig. 1 but is bleached in spectra (iii) and (iv), where the optical response is dominated by reflection from the alumina. It would be very surprising to find that the absorption feature the authors of the Comment attribute to the alumina decreases in intensity with increasing *n*-type doping in the same way as shown in Fig. 1 and increases in energy with decreasing pore size.

III. REPPERT *et al.* SAMPLES

For their experiments, Reppert *et al.* used FTIR Grade 99+% KBr powder purchased from Thermo Spectra-Tech (CAS# 7758-02-3).[5] The Bi nanorods in this KBr matrix were measured in transmission mode and referenced to an open hole in the FTIR spectrometer. Hence, in our experiments we also measured their sample in transmission mode, referenced against an open hole in our FTIR spectrometer.

We feel confident that the measured absorption vs wave number observed for these samples does not originate from impurities in the KBr pellet for several reasons. As can be seen in Fig. 2, reference samples of both KBr and bulk Bi (labeled as Bi powder) were also recorded using the same background spectrum and no absorption features mentioned by the authors of the Comment were observed.[6] The measured spectra of their KBr pellets do not show an optical feature near the energy of the bismuth optical feature reported in Ref. 8. Furthermore, as seen in Ref. 8, if nitrogen impurities did indeed exist in their KBr, then they would observe not only the peak at 1387 cm^{-1} but also all the other dominant peaks corresponding to nitrogen impurities. Therefore, the optical-absorption features measured in these samples cannot be a result of nitrate impurities in the KBr
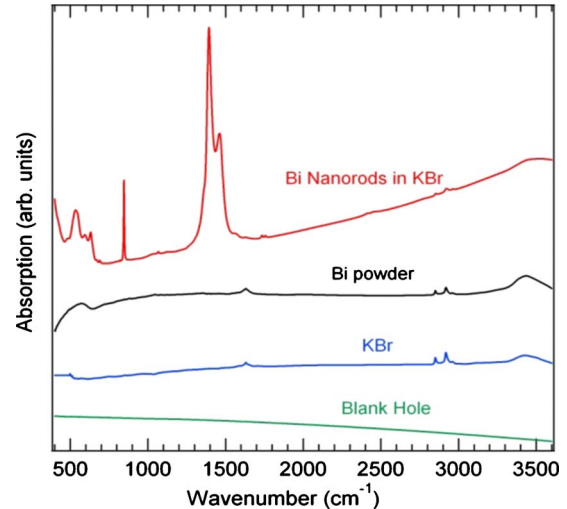

FIG. 2. (Color online) FTIR absorption vs wave number spectra of Bi nanorods in KBr, Bi powder, KBr, and the blank hole in the FTIR spectrometer, all referenced to the blank hole (Refs. 6 and 7). The spectra are offset for clarity purposes.

pellets. Finally, Reppert *et al.*[7] conducted these same experiments at 77 K, which would have enhanced the contributions to the spectra from any existing impurities. Details of the experimental setup used by Reppert *et al.* may be found in Refs. 5 and 6.

IV. CORNELIUS *et al.* SAMPLES

The authors of the Comment raise the question of the wire density in the third set of samples, prepared by Cornelius *et al.* These samples were prepared by the same method and by the same scientist as in Ref. 9 and we therefore assumed that the wire density was similar. Moreover, we note that the reflectance spectra we measured from many different spots on the sample looked qualitatively similar and did not display the large absorption feature observed in the Bi nanowire samples of the other two groups. However, without knowing the wire density of this sample, we cannot rule out the possibility that we did not observe the large absorption feature due to insufficient sensitivity in our experimental setup.

For our study, we measured the samples in reflectance mode, using background spectra from both a gold mirror and a highly reflective silicon wafer. We chose to only include data using the gold background in our paper since this provided a flatter baseline and is therefore a more accurate background spectrum, and also because silicon has some small characteristic features in the selected energy range. However, the results using both backgrounds were very similar, so we have no reason to question the data from Ref. 9.

The experimental setup we used throughout our experiment is the same as in Ref. 1. Without a polarizer in place, the incident light was unpolarized. The Nicolet product website lists all relevant details on the setup geometry, which is a standard one for such experiments. It goes without saying that the plots we included in the paper were meant to be representative. We made sure that each of these scans was

reproducible and looked very similar to scans taken on other regions of the sample.

V. CLOSING COMMENTS

The identification of the absorption peak near 1000 cm^{-1} in bismuth nanowires has been studied quite extensively and is described in other publications.[1,10] The optical absorption in bismuth nanowires was measured as a function of diameter, doping, and polarization.[1] The energy of the peak increases with decreasing diameter, by an amount very close to that predicted by theory due to quantum confinement at the L and T points.[2] Likewise, the doping dependence supports the theory that the optical-absorption feature is the result of an electronic transition between the L and T points. The polarization dependence also supports this theory since this optical feature disappears when the incident light is polarized parallel to the nanowire axis. Finally, numerical simulations qualitatively reproduce the dependence of the energy and intensity of this observed optical feature on the various factors mentioned above.[1]

As with all science, we can never be completely confident that our theoretical analysis is correct; we can only make predictions and test our theories under new circumstances. So far, our theory—namely, that the strong optical absorption feature near 1000 cm^{-1} in bismuth nanowires (average diameter ~45 nm) can be attributed to an indirect L to T point valence band transition—has shown good agreement with the line shape and with the dependencies on doping, polarization, diameter, and crystalline orientation. Additional experiments that may shed light on the scope and validity of this theory include single-wire measurements and magneto-optical measurements of nanowire arrays, as well as studies of the temperature dependence of these absorption features. Furthermore, we note that the temperature dependence of band parameters that we have used in our model has only been measured for bulk bismuth,[11] and our assumption that it holds true for bismuth nanowires as well may require experimental verification. However, we do not see how the optical absorption from either the KBr pellet or the anodic alumina template could result in the optical spectra reported in Ref. 2 and in several other previous publications (e.g., Refs. 1, 5, and 6).

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