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Phonons in ZnTe/CdSe superlattices with interchange of cation layers across interfaces

Zhi-Zhong Xu†§, Heather Dowd†, Shang-Fen Ren†‖ and Zong-Quan Gu‡

† Department of Physics, Illinois State University, Normal, IL 61790-4560, USA

‡ State Key Laboratory for Surface Physics, Institute of Physics and Center for Condensed Matter Physics, Academia Sinica, Beijing, People's Republic of China

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Abstract. The ZnTe/CdSe superlattice is one of the wide-gap semiconductor superlattices grown successfully in recent years which have potential applications in blue–green diode lasers. There exists experimental evidence of interchange of entire atom layers across the interfaces of ZnTe/CdSe superlattices in spite of the resulting interface strain. First-principles pseudopotential calculations of the total energy of such systems confirmed the possibility of such interchanges. By using the combination of a first-principles pseudopotential method and an empirical method with parameters extracted from the available experimental data and pseudopotential calculations, we studied phonons in ZnTe/CdSe superlattices with interchange of atom layers across the interface. The results are compared with phonons in ZnTe/CdSe superlattices with ideal interfaces. Several unique features of phonon modes in superlattices with interchange of atomic layers across interfaces are identified and discussed. These results provide more information about interface structures in such heterostructures, and we hope that they will stimulate more experimental measurements in these materials.

1. Introduction

ZnTe/CdSe superlattices, which have potential applications in blue–green diode lasers, have been grown successfully in recent years [1, 2]. One important feature of such superlattices is that they are lattice matched. The lattice constants of CdSe and ZnTe are 6.077 Å and 6.099 Å, respectively, so the mismatch is less than 0.3%. Because of the closely matched lattice constants, one expects negligible strain at interfaces, thus allowing high-quality superlattices with ideal and sharp interfaces to be grown. However, another feature of ZnTe/CdSe superlattices is that the two constituent materials, ZnTe and CdSe, do not share a common atom, so there are two different interfaces, ZnSe-like and CdTe-like, in such superlattices. Because the lattice constants of ZnSe and CdTe are 5.668 Å and 6.482 Å respectively, which are quite different from ZnTe and CdSe, substantial biaxial intrinsic strains exist at the interfaces in such superlattices even though they are lattice matched.

There exist experimental observations of interface reconstructions in ZnTe/CdSe heterostructures. Close examination of high-resolution transmission electronic microscopic (TEM) spectra showed that there exist two to three layers of reconstructions at interfaces in such superlattices [1]. Extended x-ray absorption fine-structure (EXAFS) studies of such interfaces indicated the existence of interchanges of entire atomic layers across the interfaces

§ Permanent address: Department of Physics, Fudan University, Shanghai, People's Republic of China.

‖ Corresponding author. E-mail address: ren@silicon.phy.ilstu.edu

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[2]. *Ab initio* pseudopotential calculations of the total energy of ZnTe/CdSe superlattices [3] confirmed the possibility of interchanging atomic layers across the interfaces. It also suggested that superlattices with interchange of cation layers across both interfaces have the lowest total energy [3].

Here we performed calculations of phonons in ZnTe/CdSe superlattices with ideal interfaces and those with interchange of atomic layers across the interfaces. The results of phonons with wavevectors in the growth direction in superlattices with interchange of cation layers across interfaces will be shown and discussed in detail here. For convenience of later discussions, we will define a few terms here. We use IDIF to indicate an ideal interface, ICIF to indicate an interface with interchange of cation layers across the interface, IDSL to indicate superlattices with ideal interfaces and ICSL to indicate superlattices with interchange of cation layers across interfaces.

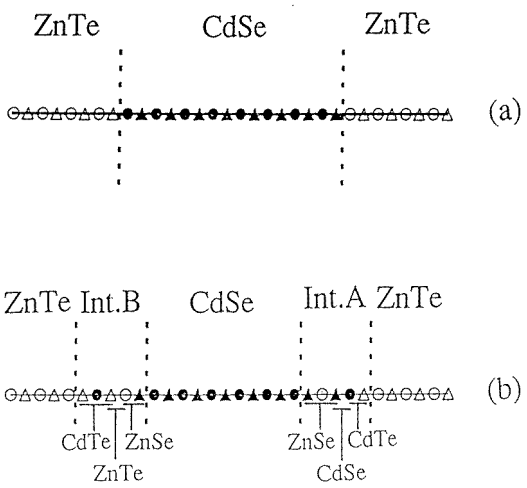

Figure 1. Structures of $(ZnTe)_8(CdSe)_8$ superlattices with ideal interfaces (a) and with interchange of cation layers across the interfaces (b).

The structure of a $(ZnTe)_8(CdSe)_8$ superlattice with an ideal interface (IDSL) is shown in figure 1(a), where two types of interface, ZnSe-like and CdTe-like, are indicated. The structure of the same superlattice with interchange of cation layer across both interfaces (ICSL) is shown in figure 1(b). By looking at the structures of these two superlattices, we noticed several features unique in ICSL.

First, in ICSL, the two constituent materials (ZnTe and CdSe) not only exist in the bulk form, but also exist at the interfaces (see the CdSe layer at the interface A, and the ZnTe layer at interface B in figure 1(b)). Second, both interface materials (CdTe and ZnSe) exist at both interfaces (interface A and interface B), so each type of interface now has both CdTe-like and ZnSe-like layers, but with different thickness (see the Cd layer next to the Te layer and the two Se layers on each side of Zn layer at interface A, and the Zn layer next to the Se layer and two Te layers on each side of the Cd layer at interface B). These two features do not exist in IDSL, so they will cause differences of phonons between ICSL and IDSL, which we will discuss in detail later.

This article is organized as follows. In section 2 we will give a brief description of the theoretical approach we used, in section 3 we show our results and give discussions and section 4 is a conclusion.

2. Theoretical approach

In our calculations, two theoretical approaches are used. First, we used a first-principles pseudopotential method to calculate the total energy and force constants in cubic CdSe [3], because CdSe is a wurtzite structure in nature but a zincblende structure in ZnTe/CdSe superlattices [4]. Then we used an empirical method with parameters extracted from the first-principles pseudopotential method for cubic CdSe and the experimental data for ZnTe, CdTe and ZnSe [5]. In this empirical approach, the total interaction between atoms is considered as two parts, the long-range Coulomb interaction and the short-range interaction [6–9]. The long-range Coulomb interaction is calculated by using the approach discussed in detail in [8], with different layer distances at interfaces due to the strain considered. The short-range interactions are considered up to the second neighbours, and they are calculated by using a valence force field model [10], where the energy changes due to phonon vibrations are considered as two parts, one due to the bond-length changes and one due to the bond-angle changes.

Table 1. The calculated and measured phonon frequencies of four bulk materials ZnTe, CdSe, ZnSe and CdTe, where the results listed in parentheses for ZnTe, ZnSe and CdTe are experimental results taken from [5], and the results listed in parentheses for cubic CdSe are from an *ab initio* pseudopotential calculation [3]. All the frequencies listed are in the unit of THz.

	ZnTe	CdSe	ZnSe	CdTe
LO(Γ)	6.20 (6.20)	7.39 (7.48)	7.42 (7.50)	4.86 (5.05)
TO(Γ)	5.39 (5.30)	6.50 (6.40)	6.22 (6.20)	4.57 (4.20)
LO(X)	5.25 (5.51)	6.44 (6.44)	6.12 (6.20)	4.00 (4.04)
TO(X)	4.86 (5.21)	7.05 (7.05)	6.84 (6.70)	4.17 (4.44)
LA(X)	4.06 (4.29)	5.08 (5.05)	5.23 (5.70)	3.06 (3.50)
TA(X)	1.76 (1.62)	1.43 (1.55)	2.01 (2.10)	1.67 (1.05)

In table 1 we listed our calculated results of phonons for four materials, ZnTe, CdSe, ZnSe and CdTe, by using this approach. These four materials are related to ZnTe/CdSe superlattices in that ZnTe and CdSe are two bulk materials, and ZnSe and CdTe are two interface materials. For comparison the corresponding experimental data for three of these materials are listed in the same table, as well as the first-principles calculations for the cubic CdSe.

3. Results and discussions

We have calculated all phonon modes in an IDSL and an ICSL of $(ZnTe)_8(CdSe)_8$ and investigated the vibrational amplitudes of different modes. Next we will discuss a few features of these modes.

In figure 2 we show the frequency ranges of ZnTe/CdSe superlattices and the related bulk materials. In the middle panel of this figure is the frequency range of ZnTe/CdSe superlattices, which is derived from the frequency ranges of four related materials, shown on the left. The superlattice phonons are labelled as LA, LO, TA and TO according to their frequency ranges in bulk materials, where L (T) represents longitudinal (transverse) modes, and A (O) represents acoustic (optical) modes, respectively. The calculated frequencies for $(ZnTe)_8(CdSe)_8$ IDSL and ICSL at the centre of the Brillouin zone as the wavevector approaches zero in the growth direction are shown on the right (it is important to point out

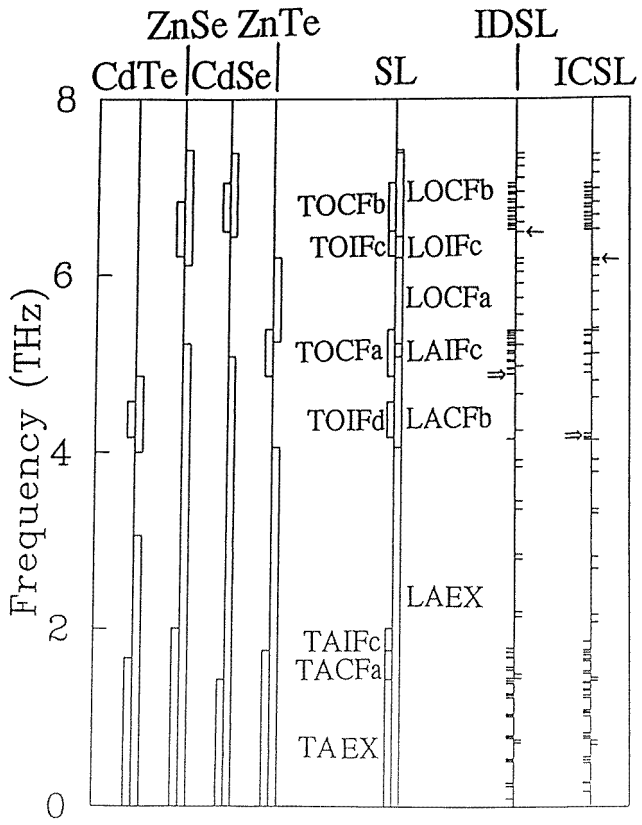

Figure 2. The middle panel of this figure is phonon frequency ranges of the ZnTe/CdSe superlattice, where the letter a, b, c, d after the modes indicates one of the four materials: a is for ZnTe; b is for CdSe; c is for ZnSe and d is for CdTe. On the left are phonon frequency ranges of ZnTe, CdSe, ZnSe and CdTe, and on the right are calculated phonon frequencies of an IDSL and an ICSL of $(ZnTe)_8(CdSe)_8$.

this because of the anisotropic behaviour of optical phonons at the centre of the Brillouin zone in such materials [6, 7]). For each material, the longitudinal modes are on the right and the transverse modes are on the left. According to phonon frequency ranges in the four bulk materials, the phonon frequency range in superlattices is divided into several different zones, such as extended zones (EX), which are frequency ranges shared by both ZnTe and CdSe, and confined zones (CF), which are frequency ranges for either CdSe or ZnTe. In a frequency range which belongs to neither CdSe nor ZnTe but belongs to CdTe or ZnSe, there will exist interface phonon zones (IF), either CdTe-like or ZnSe-like. It is expected that in the EX zone, the phonon vibrations will be extended to both ZnTe and CdSe, and in the CF zone, the phonon vibration will be mainly confined in one material, either in CdSe or in ZnTe. In the IF zone, it is either CdTe-like or ZnSe-like, and localized at the corresponding layers.

Comparing phonon frequencies in $(ZnTe)_8(CdSe)_8$ IDSL and ICSL shown on the right of figure 2, we see that most frequencies stay about the same, but three change substantially, which are indicated by arrows (the double arrows indicate two degenerate or very close frequencies). The vibrational amplitudes of these three modes are shown in figure 3, where

the left panel corresponds to the three modes of IDSL, and the right panel corresponds to the three modes of ICSL. Figure 3(a) is a longitudinal mode, which shows that a LOCF(CdSe) mode in IDSL turns into a LOIF(ZnSe) mode in ICSL, with the frequency changed from 6.48 THz in IDSL to 6.16 THz in ICSL. Figures 3(b) and (c) are two transverse modes, which show that two TOCF(ZnTe) modes in IDSL are changed into two TOIF(CdTe) modes in ICSL. Their frequencies are changed from two almost degenerate ones of about 4.88 THz in IDSL to 4.16 THz and 4.20 THz in ICSL respectively. From figure 1 we see that there are more interface layers in ICSL than in IDSL, which leads to the increase in the number of IF modes in ICSL, so some CF modes in IDSL are changed into IF modes in ICSL, and their frequencies also change substantially.

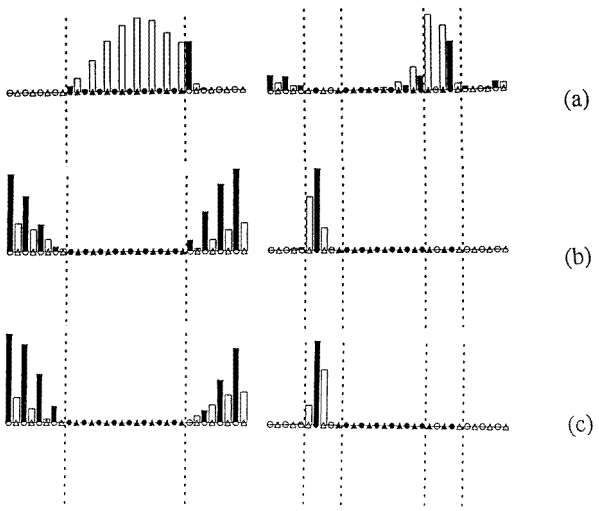

Figure 3. Vibrational amplitudes of three modes changed from CF modes in IDSL (on the left) to IF modes in ICSL (on the right). Each interface in IDSL is indicated by one dashed line, and each interface in ICSL are indicated by two dashed lines. The black circles, black triangles, white circles and white triangles are for Cd, Se, Zn and Te layers, and the black and white columns are for the vibrational amplitudes of cation and anion layers. (a) is a longitudinal mode with the frequency of 6.48 THz for IDSL and 6.16 THz for ICSL; (b) and (c) are two transverse modes with two almost degenerate frequencies of 4.88 THz for IDSL and 4.16 and 4.20 THz for ICSL.

Next we will show some typical results for a few other confined modes and interface modes in ICSL. The discussions are for wavevectors in the growth direction (z-direction). Even though the results shown here are for $k_z \to 0$, the results for k_z of other values are similar.

3.1. Confined acoustic (LACF and TACF) modes

In figure 2 we see that for ZnTe/CdSe superlattices the confined acoustic modes exist in two frequency ranges, LACF(CdSe) and TACF(ZnTe), where, according to the notation we introduced above, LACF (TACF) represents confined longitudinal (transverse) acoustic modes. The first range is fully or partially overlapped with the LO frequency range of CdTe and LA frequency range of ZnSe, and the second range is fully or partially overlapped with the TA frequency ranges of CdTe and ZnSe. In figure 4 we show the vibrational amplitudes

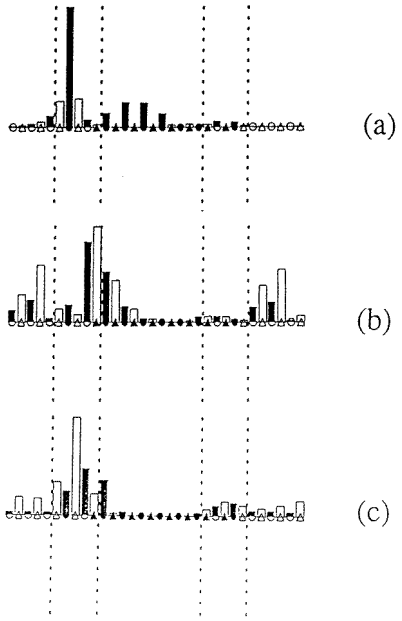

Figure 4. Vibrational amplitudes of three confined acoustic modes with frequencies 4.80 THz (a), 1.49 THz (b) and 1.70 THz (c) in an ICSL of $(ZnTe)_8(CdSe)_8$ where (a) is a longitudinal mode, and (b) and (c) are transverse modes. The symbols are the same as in figure 3.

for one longitudinal and two transverse modes in these two frequency ranges. Figure 4(a) is for a longitudinal mode with a frequency of 4.80 THz, which is in the range of LACF(CdSe) overlapped with the LO frequency range of CdTe and ZnSe. This mode shows the characters of both LACF(CdSe) and LOIF(CdTe), i.e. it shows the character of a confined CdSe mode, and it also shows the character of an interface mode of CdTe at interface B. Figures 4(b) and (c) are for two transverse modes with the frequencies of 1.49 THz and 1.70 THz respectively, which are in the frequency range of TACF(ZnTe) overlapped with the TA frequency range of ZnSe. The mode shown in figure 4(b) is located both in ZnTe layers and at the ZnSe interface layer. But the mode shown in figure 4(c) is mainly confined in the ZnTe layer between the CdTe layer and the ZnSe layer at the interface B. We want to point out the fact that ZnTe, which is one of the two constituent materials of the superlattice, also exists at the interface, which is a unique feature of ZnTe/CdSe ICSL, as we discussed earlier. So the confined ZnTe mode at the interface layer is a unique feature of phonons in such superlattices. Similarly, another constituent material, CdSe, also exists between two different interface layers at the other interface.

3.2. Confined optical (LOCF and TOCF) modes

In figure 2 we see that, for CdSe/ZnTe superlattices, there are four frequency ranges for confined optical modes, which are LOCF(ZnTe), LOCF(CdSe), TOCF(ZnTe) and TOCF(CdSe). Among these modes, LOCF(ZnTe) and TOCF(ZnTe) modes have almost no overlap with others, but LOCF(CdSe) and TOCF(CdSe) have overlap with LO and TO frequency ranges of ZnSe respectively. Because the frequency ranges of optical phonons are quite different for different materials, the confined optical modes can be understood as

energy levels in quantum wells. The width of the quantum well is the thickness of this material. As we pointed out at the beginning of this section, the two constituent materials, ZnTe and CdSe, exist in two forms in such superlattices, one as a constituent material of the superlattice with many layers, and another at the interfaces with very thin layers. Because the thicknesses of these two forms are quite different, the confined optical modes exist in only one of these two forms of layers but not in both. Figure 5(a) ((b)) shows a longitudinal (transverse) mode with a frequency of 5.59 THz (5.23 THz), which is in the range of LOCF(ZnTe) (TOCF(ZnTe)). These two figures show the confined mode in either of the two forms of ZnTe layers, as discussed above.

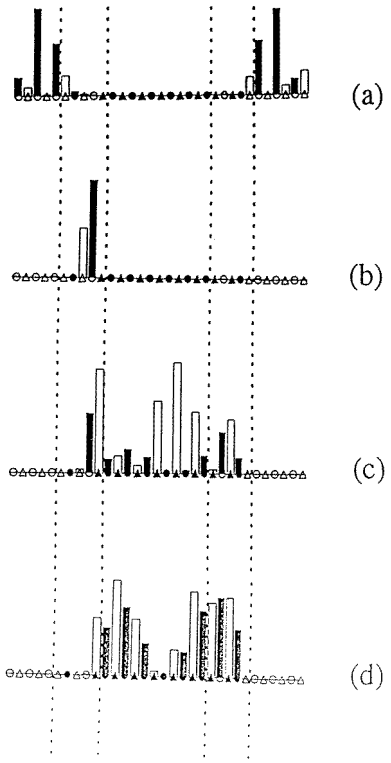

Figure 5. Vibrational amplitudes of four confined optical modes with frequencies 5.59 THz (a), 5.23 THz (b), 6.67 THz (c) and 6.99 THz (d) in an ICSL of $(ZnTe)_8(CdSe)_8$, where (a), (c) are longitudinal modes, and (b) and (d) are transverse modes. The symbols are the same as in figure 3.

However, in the frequency ranges of LOCF(CdSe) and TOCF(CdSe) which are overlapped with LO and TO frequency ranges of ZnSe respectively, the situation is different. Through the media of LOIF(ZnSe) and TOIF(ZnSe), it is possible that the confined optical modes have large vibrational amplitude both in the bulk layers and at the interface layers. This can be seen from figures 5(c) and 5(d), which are for a longitudinal mode at the frequency of 6.67 THz and a transverse mode at the frequency of 6.99 THz. There are large vibrational amplitudes in both the bulk CdSe layers and the interface CdSe layer.

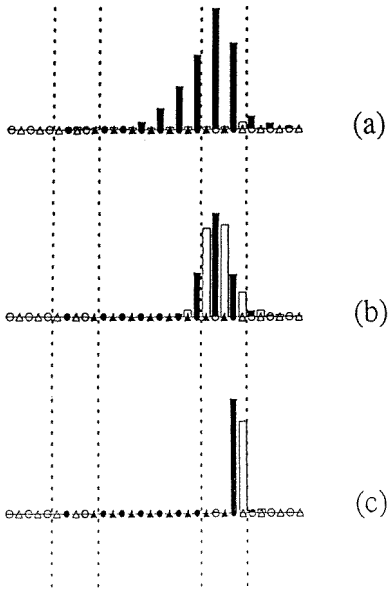

Figure 6. Vibrational amplitudes of two interface acoustic modes with frequencies 5.10 THz (a) and 1.86 THz (b) and the interface optical mode with the frequency of 4.14 THz (c), where (a) is a longitudinal mode, and (b) and (c) are transverse modes. The symbols are the same as in figure 3.

3.3. Acoustic interface (LAIF and TAIF) modes

There are two acoustic interface modes appearing in the ranges of LAIF(ZnSe) and TAIF(ZnSe) respectively, with the frequencies of 5.10 THz and 1.86 THz. The vibrational amplitudes of these two modes are shown in figures 6(a) and (b). It is obvious that these two amplitudes are localized at the interface ZnSe layer and decay on both sides.

3.4. Optical interface (LOIF and TOIF) modes

In this range we identified three modes of TOIF(CdTe) with the frequency of 4.14 THz, 4.16 THz and 4.20 THz respectively. The vibrational amplitude of the first one is shown in figure 6(c), and that of the latter two have already been shown in figure 3 (the right panel of figures 3(b) and (c)) which are changed from TOIF(ZnTe) in IDSL to TOIF(CdTe) in ICSL. As we discussed at the beginning of this section, because CdTe layers exist at both interfaces in ICSL, the CdTe-like mode could be at both interfaces. However, because of the different thickness of CdTe layers at both interfaces, as we have discussed before, the interface modes will not appear at both interfaces but only at one interface at a certain frequency.

4. Conclusion

In conclusion we have calculated phonon modes in IDSL and ICSL of $(ZnTe)_8(CdSe)_8$. The results of IDSL and ICSL are compared, and several unique features of phonon modes of ICSL different from those of IDSL are identified. These features are related to the interface

structures of the superlattices. In IDSL, there are two different types of interface, ZnSe-like and CdTe-like. In ICSL, because of the interchange of cation layers at interfaces, both the above two types of interface will have ZnTe and CdSe bulk layers, and both interfaces will have ZnSe-like and CdTe-like interface layers. This makes the two different types of interface more symmetrical and brings new features on interface phonons. First, the confined bulk optical modes will appear not only in the bulk layers but also at the interface bulklike layers. However, because of the different thickness of these two types of bulk layer, the confined optical modes will only exist in either one type of bulk layer with a certain frequency but not in both. Secondly, both types of interface include two interface materials, ZnSe-like and CdTe-like layers with the interchanges, so both types of interface mode (ZnSe-like and CdTe-like) can appear at both interfaces.

Since these results are calculated by using an empirical model, the exact frequencies of the superlattice phonons are more or less parameter dependent. But the unique qualitative features of phonon modes in ICSL and IDSL discussed above are parameter independent. Our calculations with slightly different parameters for the same superlattice agree with this. We have also calculated phonon modes in IDSL and ICSL of $(InAs)_8(AlSb)_8$ superlattices, which are made from two totally different materials but have similar interface structures (two different interfaces). We obtained similar results. So these results are model independent, and they are experimentally detectable. These results provide more information about interface structures in ZnTe/CdSe superlattices, and we hope that our calculations can stimulate more experimental measurements in such materials.

Acknowledgments

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