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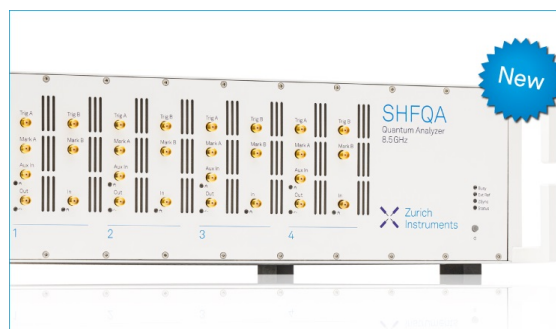
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ABSTRACT

We investigate WSe_2 – MoSe_2 heterobilayers with different twist angles $\theta \pm \delta$ between the two layers by low-frequency Raman scattering. In sufficiently aligned samples with $\theta = 0^\circ$ or $\theta = 60^\circ$ and $\delta \lesssim 3^\circ$, we observe an interlayer shear mode (ISM), which is a clear sign of a commensurate bilayer structure, i.e., the layers must undergo an atomic reconstruction to form R-type or H-type stacking orders. We find slightly different ISM energies of about 18 cm^{-1} and 17 cm^{-1} for H-type and R-type reconstructions, respectively, independent of the exact value of $\theta \pm \delta$. Our findings are corroborated by the fact that the ISM is not observed in samples with twist angles, which deviate by $\delta > 3^\circ$ from 0° or 60° . This is expected since, in such incommensurate structures, with the possibility of Moiré-lattice formation, there is no restoring force for an ISM. Furthermore, we observe the ISM even in sufficiently aligned heterobilayers, which are encapsulated in hexagonal Boron nitride. This is particularly relevant for the characterization of high-quality heterostructure devices.

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The great appeal of van-der-Waals materials is the possibility to fabricate artificial multilayer structures, consisting of different materials, with arbitrary but well-controlled relative crystal orientations.¹ This offers new and, in some cases, unexpected functionalities.² Within the huge family of van-der-Waals materials, semiconducting transition-metal dichalcogenides (TMDCs) have attracted tremendous attention during the past decade.^{3,4} In the monolayer form, most of them represent direct-bandgap semiconductors⁵ with huge exciton binding energies,⁶ oscillator strengths,⁷ and spin-valley locking.^{8,9} In recent years, heterobilayer structures with staggered type-II band edge alignment^{10–12} have attracted considerable interest since, in those structures, interlayer excitons can form^{13–16} due to fast charge separation of optically excited electron–hole pairs into the two constituent layers. For momentum-allowed interlayer transitions, the two constituent layers have to be crystallographically aligned, either in the H-type stacking configuration, where the layers are rotated by $\theta = 60^\circ$ relative to each other, or in R-type stacking with $\theta = 0^\circ$. Very recently, a strong focus in this research area has been on the exploration of

possible Moiré-superlattice effects on interlayer excitons in heterobilayer structures.^{17–22} Due to the different lattice constants of the constituent materials in heterobilayers, Moiré structures are expected to form even for perfectly aligned structures, if rigid lattices of the constituent layers are assumed.²³ Moreover, the Moiré-lattice period would decrease very quickly with increasing twist-angle deviation δ from $\theta = 0^\circ$ or 60° and would be smaller than the diameter of an interlayer exciton in, e.g., a WSe_2 – MoSe_2 heterobilayer, of typically 3–4 nm, for $\delta \gtrsim 5^\circ$.

Intriguingly, very recently, it has been shown via conductive atomic force microscopy²⁴ and transmission electron microscopy²⁵ that in TMDC heterobilayers^{24,25} and homobilayers,²⁵ atomic reconstruction takes place, where the atoms in the two constituent layers arrange as in R- or H-type homobilayers, for deviations $\delta \leq 1^\circ$ (as reported in Ref. 24) or $\delta < 3^\circ$ (cf. Ref. 25) from $\theta = 0^\circ$ or $\theta = 60^\circ$. We note that similar reconstructions are also reported for bilayer graphene.²⁶ Assuming rigid lattices of the constituent layers, Moiré superlattices would form in these cases. However, in Refs. 24 and 25, it was

found that the bilayers reconstruct in domains with H-type or R-type stacking configurations, i.e., in the commensurate lattice configurations of perfectly aligned homobilayers. The domain formation was theoretically predicted for the first time in Ref. 27 via conformational considerations, and indeed, density functional theory calculations confirmed that in the above cases, the two stacking configurations are the energetically favorable lattice arrangements^{24,25,28,29} (also see Ref. 30 for a classical modeling). For R-type stacking, two energetically degenerate commensurate configurations are possible for a heterobilayer [see Fig. 1(c)], whereas the H-type stacking has only one energetically favorable lattice arrangement [displayed in Fig. 1(d)]. In the recently published experimental and theoretical works,^{24,25} it is reported that for R-type reconstruction, triangular domains form with the two degenerate AB and BA lattice configurations [see Fig. 1(c) for illustration]. For the H-type atomic reconstruction, the domains have a hexagonal shape, as illustrated in Fig. 1(d). The size of the domains

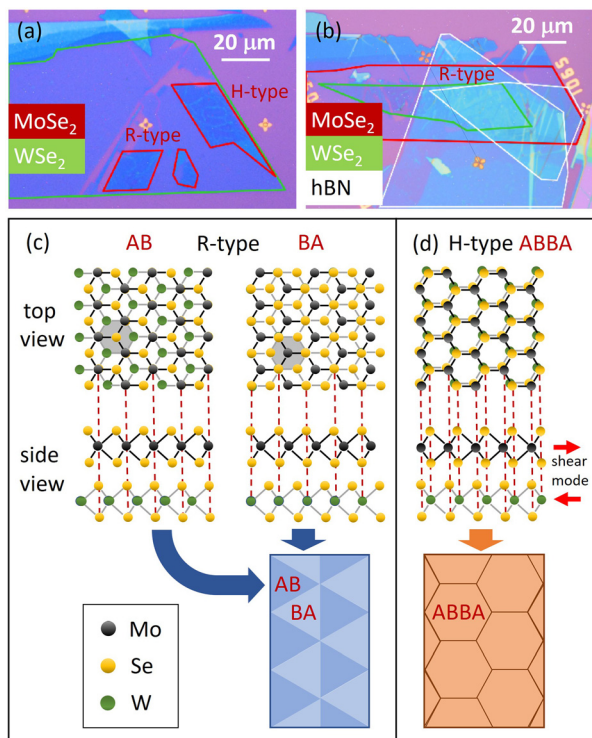


FIG. 1. (a) Microscope image of an investigated heterobilayer sample. The red and green lines mark the MoSe₂ and WSe₂ monolayer regions, respectively. (b) Microscope image of a heterobilayer, encapsulated in hBN layers, which are outlined by white lines. (c) Left: schematic of the atomic arrangement in an AB reconstructed R-type heterobilayer, where the metal atom (A) in the upper layer is above the chalcogens (B) in the lower layer. Right: the same for the energetically equivalent BA reconstructed R-type structure, where the chalcogens (B) in the upper layer are above the metal atoms (A) in the lower layer. The gray-shaded hexagon marks the same unit cell of the lower layer, while the upper layer is fixed. The lower panel shows the expected triangular domain pattern with AB- and BA R-type domains, as reported in Ref. 24. (d) Atomic arrangement of a reconstructed ABBA H-type heterobilayer, where the upper layer is rotated by 60° with respect to the lower one. The movement of the layers in the interlayer shear mode is indicated by red arrows. The lower panel shows a schematic picture of the expected hexagonal domain structure with ABBA atomic reconstruction.²⁴

depends on the deviation angle δ , it is in the range of several tens to one hundred nanometers.²⁴

Raman spectroscopy is an important noninvasive tool in materials science. It has been very successfully applied to graphene³¹ and many other single- and multi-layered van-der-Waals materials. For an overview of Raman experiments on TMDCs, see, e.g., the review articles in Refs. 32–34 and references therein. The first observation of interlayer shear modes (ISMs) in TMDC multilayers was reported by Plechinger *et al.*³⁵ for MoS₂. Most importantly, for the existence of an ISM, a restoring force for the rigid layer displacement is required. Therefore, so far, bilayer ISM has only been observed in homobilayers with R-type or H-type stacking since, there, a restoring force for the ISM is present^{36–38} due to the atomic registry of the commensurate equal lattices. For twist angles θ other than 0° or 60°^{37,38} or for heterobilayers³⁶ and heteromultilayers,³⁹ where there is no restoring force for an ISM expected, only interlayer breathing modes (IBMs) are reported so far for room-temperature experiments.^{36–39} For breathing modes, the van-der-Waals force between the layers plays the role of the restoring force.

In this work, we employ low-frequency Raman scattering (LFRS) for the investigation of WSe₂-MoSe₂ heterobilayers with different twist angles. In sufficiently aligned heterobilayers, we observe an ISM, which is clear evidence for a commensurate lattice arrangement, as provided by R-type and by H-type stackings. Very interestingly, we find slightly different ISM energies for H-type and R-type reconstructions, which offer the perspective of optical identification of these atomic reconstructions via contactless LFRS experiments. Furthermore, we observe the ISM even in sufficiently aligned heterobilayers, which are encapsulated in hexagonal Boron nitride (hBN). These results show the potential to identify commensurate stacking configurations even in buried heterostructures by noninvasive, contactless LFRS.

The Raman experiments are performed using an optical scanning-microscope setup at room temperature under ambient conditions. For excitation, a 532 nm laser line with an output power of 2.5 mW is used. The laser is focused to a spot of $\sim 1 \mu\text{m}$ diameter by a 100× microscope objective. For stray-light reduction, we use a Bragg-filter set. The spectra are analyzed using a grating spectrometer, and a Peltier-cooled CCD camera is used for detection.

The heterostructure samples are prepared on silicon wafers with a SiO₂ layer via mechanical exfoliation, using Nitto tape, and a deterministic all-dry transfer technique,⁴⁰ employing polydimethylsiloxane (PDMS) stamps. Figure 1(a) shows a microscope image of one of the bare heterobilayer samples, investigated in this work. In Fig. 1(b), an image of one of two hBN-encapsulated heterobilayers, investigated in this work, is displayed.

For identification of 0° and 60° alignment in the first place, we use measurements of the interlayer-exciton g factors via photoluminescence (PL) spectroscopy in high magnetic fields⁴¹ (cf. Ref. 21). Correspondingly, we identify heterobilayers, for which we measure g factors, ranging from 2.5 to 5.2, with 0° alignment (R-type stacking), and, ranging from −16.8 to −14.7, with 60° alignment (H-type stacking), largely consistent with experiments in Ref. 21 and theoretical considerations in Ref. 28. As will be shown below, an important result of the present work is that the orientation (0° or 60°) can be determined by the energy of the ISM, if atomic reconstruction has taken place. We note that these results coincide perfectly with our assignments from magneto PL.

We begin our discussion by comparing spectra of two exfoliated homobilayers with those of a heterobilayer. Figure 2(a) shows linearly cross-polarized Stokes and Antistokes Raman spectra of WSe_2 - and MoSe_2 homobilayers (green and black spectra) and of a WSe_2 - MoSe_2 heterobilayer with $\theta = 60^\circ$ and $\delta \sim 3^\circ$. The spectra are not normalized but shifted vertically for better comparison. The two H-type homobilayer samples show the well-known ISM⁴² at energies of $\sim 17.7 \text{ cm}^{-1}$ and $\sim 19.2 \text{ cm}^{-1}$ for WSe_2 and MoSe_2 , respectively. We use crossed linear polarizations since the ISM is allowed in both configurations, parallel and crossed linear polarizations,^{35,42} and the laser-stray-light reduction is much better in the latter case. Surprisingly, the heterobilayer also shows a strong Raman peak, which is energetically in-between the peaks of the two homobilayers [indicated by a vertical dashed line in Fig. 2(a)]. Therefore, it is highly likely that this Raman peak at an energy of $(18.0 \pm 0.1) \text{ cm}^{-1}$ is an ISM of the heterobilayer. So far, it was argued in the literature^{36,37} that for heterobilayers with incommensurate lattice arrangements, an ISM is not possible because of the lack of a restoring force for the rigid layer displacement. However, as mentioned above, recent reports show^{24,25} that both lattices can undergo atomic reconstruction for energetic reasons, and commensurability is restored. Therefore, we interpret the Raman peak at 18 cm^{-1} in the orange spectrum in Fig. 2(a) as the ISM of the WSe_2 - MoSe_2 heterobilayer. Consequently, this measurement provides evidence for the H-type atomic reconstruction. For comparison, we plot in Fig. 2(b) Raman spectra of the same samples for unpolarized detection of the inelastically scattered light. In these spectra, the ISM peaks of all samples are reproduced, as expected from the selection rules. In addition, the IBM is visible at an energy of about 27.7 cm^{-1} in the spectrum of the WSe_2 homobilayer [green spectrum in Fig. 2(b)]. For the other two samples, the scattering probability for the IBM at

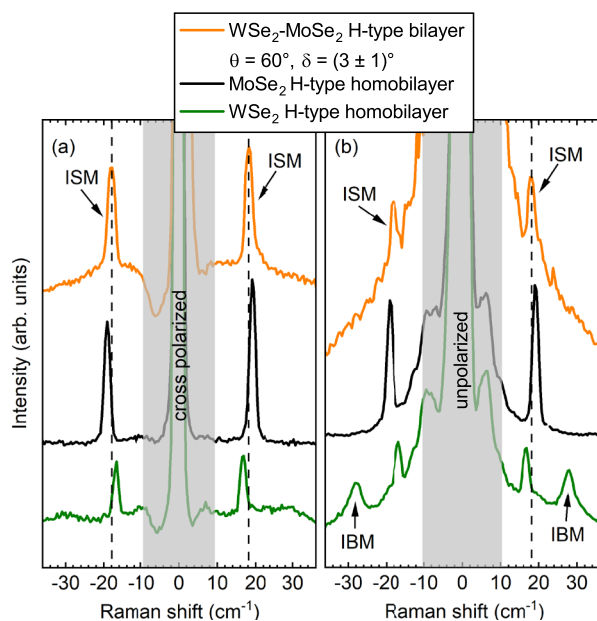


FIG. 2. (a) Cross-polarized low-frequency Stokes- and Antistokes Raman spectra of exfoliated natural (H-type) WSe_2 - and MoSe_2 homobilayers (green and black spectra, respectively) and of a WSe_2 - MoSe_2 heterobilayer with $\theta = 60^\circ$ and $\delta \sim 3^\circ$ (orange spectrum). (b) The same as (a) but for unpolarized detection.

the used laser energy is obviously too small to be observed in the measurement. One can also clearly recognize the much stronger laser stray-light signal in the unpolarized Raman spectra in Fig. 2(b). The IBM should, in principle, also exist for the heterobilayer since, for the IBM, the van-der-Waals force between the layers plays the role of a restoring force for the rigid layer breathing oscillation.³⁶ Since our focus, in this work, is the ISM, which requires commensurate lattices, for better stray-light suppression, we stay in the following with crossed-linear polarization configurations. We note that we have measured several spots (typically 3) on all investigated samples. We find very similar spectra with exactly the same ISM energy on all investigated spots of a given sample, without any exception. The spectra shown in the plots are thus representative. Therefore, we conclude that the domains, as schematically displayed in Figs. 1(c) and 1(d), may form rather homogeneously over the whole sample area although, of course, our spatial resolution is much worse than the typical domain sizes, and averaging cannot be avoided in the optical experiment.

For more detailed analysis, we show in Fig. 3(a) representative Stokes–Antistokes spectra of all investigated heterobilayers without hBN encapsulation. For a quantitative comparison, all spectra have been normalized to the intensities of the A'_1 monolayer optical phonons of the respective samples. The A'_1 phonons are at much larger Raman shifts, which is not displayed in the low-frequency spectra in Fig. 3(a). For a comparison of normalized Raman spectra also over the energy range of the optical phonons, see Fig. S1 in the [supplementary material](#). The legend of Fig. 3 contains the twist angles θ and the deviations δ in brackets, if known. If the corresponding values are not known for a sample, this is indicated by “nk.” Additionally, our interpretations of the lattice arrangements are also mentioned as H-type, R-type, or incommensurate in the legend. For most of the samples, the twist angles could be determined via second-harmonic generation microscopy.^{16,43} The procedure how the angles are determined is

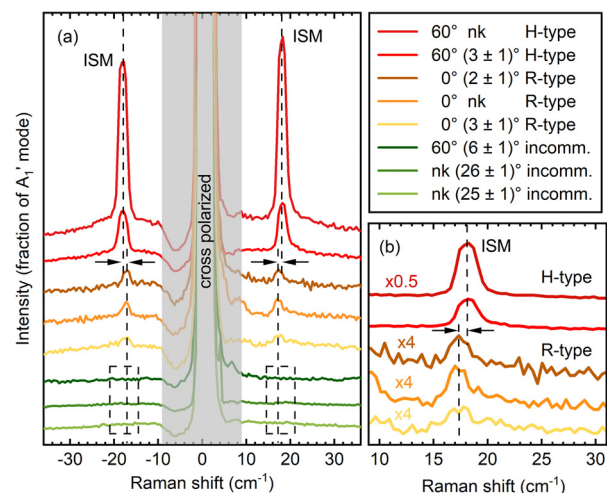


FIG. 3. (a) Representative cross-polarized low-frequency Raman spectra of eight different WSe_2 - MoSe_2 heterobilayers. The respective relative twist angles θ of the heterobilayers are given in the legend on the right-hand side. The measured deviations δ are given, together with estimated errors, in brackets. nk means “not known.” (b) Blowup of the Stokes region for the samples with lattice reconstruction. Some of the spectra are renormalized as indicated.

described in more detail in the [supplementary material](#). For an accurate determination, large enough monolayer parts of each material are required. This is not given for all samples. Therefore, some of the angles are not precisely known. For those samples we have to rely on the accuracy of parallel sample-edge alignment in the preparation processes, which is about $\pm 3^\circ$.

The important conclusions from [Fig. 3\(a\)](#) are the following: (i) an ISM is detectable for all samples with twist-angle deviation $\delta \lesssim 3^\circ$ from $\theta = 0^\circ$ or $\theta = 60^\circ$ [yellow, two orange, and two red spectra in [Fig. 3\(a\)](#)]. (ii) For $\theta = 0^\circ$ (R-type reconstruction), the intensities of the ISM are much smaller, in our measurements by a factor of about 5–10, than those for $\theta = 60^\circ$ (H-type reconstruction). (iii) The energy of the ISM for R-type reconstruction is about $(17.4 \pm 0.1) \text{ cm}^{-1}$, while for H-type reconstruction, it is $(18.0 \pm 0.1) \text{ cm}^{-1}$. (iv) For deviation angles $\delta > 3^\circ$, no ISM signal is detectable [green spectra in [Fig. 3\(a\)](#)] although the optical phonons of the constituent layers, which appear at higher Raman shifts, are measured with comparable strengths (see [supplementary material](#) Fig. S1). Findings (ii) and (iii) are consistent with the behavior of the ISM in MoSe_2 homobilayers, where, similarly, the intensity is much lower and the energy is slightly smaller for R-type than for H-type stacking.⁴⁴ The reason for this is the smaller interlayer bond polarizability for the R-type configuration.⁴⁴ To emphasize (iii)—the difference in the ISM energies for R-type and H-type reconstructions—we show in [Fig. 3\(b\)](#) a blowup of the Stokes side of the corresponding spectra. It can be clearly seen that the energies of the ISM are constant for a given configuration (R-type or H-type), irrespective of the exact deviation angle $\delta \lesssim 3^\circ$. This confirms our interpretation that the observation of an ISM in a heterobilayer sample is evidence for an atomic reconstruction: if the reconstruction takes place, the ISM has a well-defined energy. One could imagine that the intensities of the ISM in [Fig. 3\(a\)](#) are related to the deviation angle δ and, hence, to the size of the domains: the larger the δ value, the smaller are the domains, the larger is the areal fraction of the domain walls, and the smaller is the area with atomic reconstruction, where the ISM is defined. To prove such a speculative relation, more experiments on many more samples with known twist angles are required in future work.

Finally, in [Fig. 4](#), Raman spectra of two heterobilayers, which are encapsulated in hBN multilayers, are displayed. Also, in these samples,

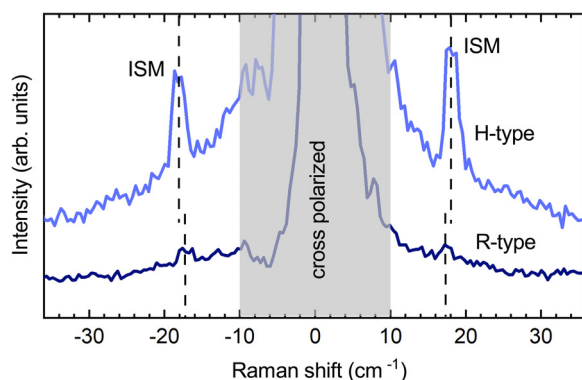


FIG. 4. Representative Raman spectra of two $\text{WS}_2\text{-MoSe}_2$ heterobilayers with $60^\circ + \delta$ (light blue spectrum) and $0^\circ + \delta$ (dark blue spectrum), which are encapsulated in hBN multilayers.

an ISM can be observed. Moreover, for both reconstructions, R-type and H-type, the energies of the ISM are the same as for the bare heterobilayer samples. Obviously, the hBN lattice is completely incommensurate with the MoSe_2 and WSe_2 lattices. Therefore, there is no restoring force interaction between the encapsulating layers and the heterobilayer, and, hence, the ISM is not disturbed by the presence of the hBN layers. The experiments in [Fig. 4](#) clearly demonstrate this effect. This is a very important further result of our investigation: even atomic reconstruction in buried heterobilayers can be detected and identified by noninvasive and contactless LFRS.

In conclusion, we have demonstrated that atomic reconstruction in TMDC heterobilayers can be detected by low-frequency Raman spectroscopy by the presence of an ISM. Even the type of reconstruction—R-type or H-type—can be identified via the energy of the ISM. An important further finding is that hBN encapsulation of the heterobilayer does not significantly influence the proposed method. The latter is very important information for the design of technologically relevant, high-quality heterostructure devices.

See the [supplementary material](#) for the Raman spectra over a broader energy range, the determination of the twist angles of the heterobilayers via second-harmonic-generation microscopy, and an overview over the investigated samples.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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