

Lattice dynamics and elastic properties of zinc-blende MgS

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Magnesium sulphide (MgS) normally crystallizes in the rocksalt structure; using a recent development in molecular beam epitaxy, it is now possible to obtain MgS in the zinc-blende structure grown on GaAs. A Raman microscope system with ultraviolet excitation at 244 nm has been used to obtain the Raman spectra of this material, revealing strong signals due to overtones of the LO and TO phonons in the backscattering geometry at room temperature. The strength of the signals implies that the excitation energy (5.08 eV) is close to resonance with the MgS band gap. Calculations of the frequency of the zone-center TO and LO phonons of this structure via *ab initio* methods are in excellent agreement with the experimental observations. The calculated and measured phonon frequencies were 433 and 425 cm^{-1} (LO) and 335 and 327 cm^{-1} (TO), respectively. Values for the lattice parameter and the elastic constants c_{11} and c_{12} of zinc-blende MgS were also obtained.

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I. INTRODUCTION

MgS is a wide-band-gap semiconductor (the band gap certainly exceeds 4.5 eV at room temperature) and it is one of the least studied members of this family. Bulk MgS crystallizes in the rocksalt (NaCl) structure, in which form it is a proposed component of interstellar dust, this identification being based on identification of its lattice vibrations in astronomical IR spectroscopy.¹ Several groups have succeeded in producing MgS in the zinc-blende (ZB) structure (often within MgS/ZnSe superlattices) by means of epitaxial growth on GaAs either by metallo-organic vapor phase epitaxy (MOVPE) (Refs. 2–4) or by molecular beam epitaxy (MBE).^{5,6} The use of ZB MgS as an extremely-wide-gap barrier material giving effectively complete confinement in II-VI quantum well structures has recently been demonstrated.⁶ However, many fundamental properties of ZB MgS remain to be determined precisely, including its lattice parameter, band gap, and band structure parameters. Here, we address the question of its lattice vibrations and elastic properties.

II. EXPERIMENT

Zinc-blende MgS layers of thickness up to 67 nm were grown on 5–10 nm thick ZnSe buffer layers on (001) GaAs substrates using a method in which a ZnS source was used together with an elemental Mg source; this yields the thickest ZB MgS obtained to date and the level of Zn incorporation is low, being in the range 0.5%–2%. The MgS epilayers were capped with a 50-nm layer of ZnSe in order to protect them from oxidation in air. Further details of the growth of the samples are given elsewhere⁶ where, in particular, double-crystal x-ray rocking curves of typical structures are presented. The lattice parameter of ZB MgS deduced in that work was 5.622 ± 0.002 Å; no evidence of conversion to the NaCl structure was seen.

The Raman spectra were acquired in a Renishaw UV Raman microscope system using 244 nm (5.08 eV) excitation from a cw frequency-doubled argon ion laser with powers of less than 0.1 mW focused via $\times 15$ or $\times 40$ objectives to spot diameters of, typically, 10 μm . Acquisition times were of the order of a few minutes and the illuminated region was inspected for damage after spectra were acquired. Experiments on similar samples using visible excitation (420 nm, 2.95 eV) with conventional macroscopic sampling did not show detectable phonon Raman spectra from the MgS layers.

III. EXPERIMENTAL RESULTS

Figure 1 shows a typical spectrum recorded from a capped zinc-blende MgS layer at room temperature. Prominent peaks at Raman shifts of 850 and 1260 cm^{-1} and a less-well-defined band with a maximum at around 1680 cm^{-1} are observed on a broad background. Also shown (lower trace) is a spectrum of a thick ZnSe epilayer on GaAs recorded under the same conditions; no signals are observed from this sample. The sharp decrease in the background signal at 500 cm^{-1} and below in the case of the MgS sample is a result of the cutoff of the bandpass filter used within the spectrometer to reject the stray laser light. As the inset in Fig. 1 shows, a further Raman band is observed at around 425 cm^{-1} , within the wavelength range blocked by the filter. The fact that this band is observable despite the attenuation of the filter suggests that this band is in reality extremely strong (around 10^4 times more intense than it appears here). Several further, much weaker features are also observed in this spectrum, including a shoulder on the dominant peak, at 752 cm^{-1} (determined by fitting after subtraction of the wing of the 2LO peak).

The two dominant bands in the spectrum have Raman shifts which are in the ratio 1.48:1 or, approximately, 3:2, and are thus assigned to 3LO and 2LO overtones of first-order LO phonon scattering. The shape of the 3LO signal is

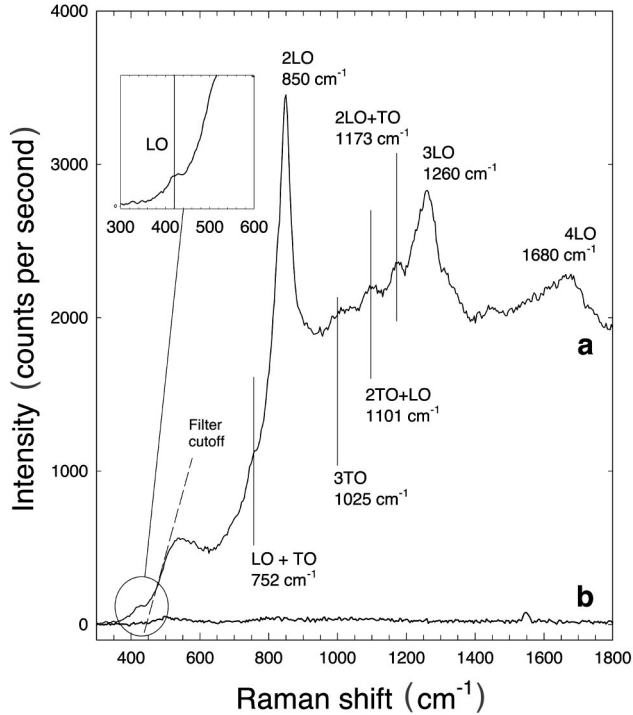


FIG. 1. (a) The Raman spectrum of epitaxial zinc-blende MgS with 5.08 eV excitation at room temperature. The inset shows the region of the spectrum below the filter cutoff on an expanded vertical scale. (b) The spectrum obtained under similar conditions from an epitaxial layer of ZnSe on GaAs, demonstrating that none of the features observed in (a) originate from the ZnSe capping layer.

strongly asymmetric, consistent with the fact that momentum conservation can be satisfied in multiple-phonon scattering by many possible combinations of non-zone-center phonons. The peak of the band near 1700 cm^{-1} can likewise be assigned to the 4LO overtone. Taking the position of the relatively sharp 2LO signal as the best indication of the zone-center LO phonon frequency, one obtains a value of 425 cm^{-1} . This is very close to the Raman shift of the strongly attenuated signal discussed above and we therefore conclude that the zone-center LO phonon frequency of zinc-blende MgS is $425 \pm 1\text{ cm}^{-1}$.

The shoulder at 752 cm^{-1} lies quite close in frequency to a mode of MgO (718 cm^{-1}),⁷ and this possible assignment is considered further below. However, a more likely assignment of this band is to combined LO+TO scattering. If we assume that it is a zone-center TO(Γ) phonon that is involved, we can infer a TO(Γ) frequency of $327 \pm 6\text{ cm}^{-1}$.

On this basis, the predicted frequencies of 3TO, 2TO+LO, and 2LO+TO overtones would be 981 cm^{-1} , 1079 cm^{-1} , and 1177 cm^{-1} , respectively, close to the other, weaker bands observed in the spectrum.

IV. CALCULATIONS

Calculations based on density functional theory (DFT) were performed using the plane-wave, pseudopotential code CASTEP.⁸ Ultrasoft pseudopotentials⁹ were used for both Mg and S atoms; for Mg, $2p$ as well as $3s$ electrons were included as valence electrons. A plane-wave cutoff energy of 380 eV was used. The Brillouin zone of the conventional cubic cell was sampled with a $4 \times 4 \times 4$ Monkhorst-Pack¹⁰ grid and equivalent \mathbf{k} -point sets were used for the other structures considered. Exchange-correlation effects were included via the local density approximation (LDA). The theoretical lattice parameter a , bulk modulus B , and elastic constants c_{11} and c_{12} were obtained from third-order polynomial fits of the variation of the total energy with dilation ($\epsilon, \epsilon, \epsilon$) and a tetragonal, volume-preserving distortion ($\epsilon, \epsilon, -2\epsilon$). Results are given in Table I, together with previous estimates. The calculated lattice parameter is in excellent agreement with experiment and the elastic constants are plausible, having magnitudes similar to those of ZnS and ZnSe.⁷ Our results differ significantly from the only other published results¹¹ (Table I) but the agreement of our calculated LO and TO phonon frequencies (see below) gives confidence also in the elastic constants presented here.

The TO phonon frequencies were obtained by applying [111] displacements appropriate for a zone-center mode to the sulphur sublattice and obtaining an effective force constant which, together with the reduced mass of the Mg and S atoms, allows one to calculate the vibrational frequency.¹² Forces were obtained for displacements ranging from 0.01 \AA to 0.1 \AA and, by fitting these to a quadratic, we extracted the harmonic contribution. The TO phonon frequency was found to be 336 cm^{-1} , which agrees well with the experimentally observed value of 327 cm^{-1} .

A supercell approach was used to calculate the zone-center LO phonon frequency.¹³ The supercell consisted of a primitive cell in the (001) basal plane and 32 atomic layers (16 Mg and 16 S) in the [001] direction. To ensure that phonons of LO symmetry were calculated, we displaced Mg or S planes separated by half of the length of the supercell by equal and opposite amounts; the displacement pattern used is shown in Fig. 2. The displacements were 0.045 \AA and the forces generated on the other Mg and S layers in the super-

TABLE I. Phonon frequencies and elastic constants of zinc-blende MgS.

	B^a	c_{11}^a	c_{12}^a	$\omega_{\text{LO}} (\text{cm}^{-1})$	$\omega_{\text{TO}} (\text{cm}^{-1})$	$a (\text{\AA})$
DFT calculation	6.12	7.40	5.47	428	336	5.615
Measured	-	-	-	425 ± 1	327 ± 6	-
Previous work	-	5.68^b	5.79^b	-	-	5.622^c

^aUnits ($10^{11}\text{ dyn cm}^{-2}$).

^bFrom Ref. 11.

^cFrom Ref. 6.

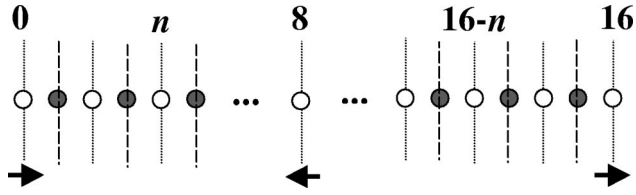


FIG. 2. Schematic view of the displacement pattern of the supercell used to calculate the LO phonon frequency (shown by the arrows). Open and solid circles represent planes of Mg and S atoms, respectively.

cell provide estimates of the planar force constants. The forces decay very rapidly away from the displaced atom, becoming negligibly small at a separation of three Mg-Mg (or S-S) layer spacings. Anharmonic effects are reduced by averaging the forces on atoms n and $16-n$, as shown in Fig. 2, when calculating the planar force constants. The zone-center LO phonon frequency is found to be 428 cm^{-1} which is again in good agreement with the experimental value of 425 cm^{-1} .

V. DISCUSSION

It is necessary to establish that the signals observed experimentally are indeed due to the MgS layer; the presence of the capping layer raises several concerns. First, it may itself give rise to Raman scattering signals. Second, since the absorption of the excitation light in the ZnSe capping layer (300 K band gap 2.7 eV) is significant, it may attenuate the excitation light or absorb the scattered light and, finally, it may even be heated by the laser to the point where damage to the epilayer occurs. This would presumably result in removal of the ZnSe capping layer and oxidation of the MgS. It was found that, even in experiments where excitation powers leading to damage were used deliberately, the Raman spectra were still dominated by the bands assigned to the ZB MgS LO phonons.

It should be noted that, if any oxidation producing MgO were to occur, the Raman spectra would be expected to be relatively insensitive to this, since MgO possesses the rocksalt structure and first-order phonon Raman scattering is therefore forbidden.¹⁴ For the same reason, Raman spectroscopy of the MgS layer itself is not expected to be very sensitive to any MgS regions possessing the rocksalt structure. We have carried out studies of bulk crystals of MgO using the same UV Raman system and have observed only much weaker phonon Raman scattering in crystals highly doped with, for instance, titanium (the doping leads to a reduction of symmetry which causes the first-order Raman bands to become detectable). The zone-center LO phonon frequencies of GaAs, ZnSe, and MgO are 292 cm^{-1} , 252 cm^{-1} , and 718 cm^{-1} respectively.⁷ Of these, the first two are outside the detection range of the equipment and the last is significantly different from any of the bands detected here and assigned to ZB MgS. As the spectrum for ZnSe shows (Fig. 1), no signals arising from ZnSe can be detected. It is therefore clear that the only layer present in the sample that can give rise to such strong Raman scattering under UV excita-

tion is indeed the zinc-blende MgS layer.

The question of the mismatch between ZB MgS and the GaAs substrate is discussed more fully elsewhere;^{5,6} the lattice mismatch strain between the two materials is of the order of 0.6%. The effect of the lattice mismatch on the Raman spectra presented here is not known precisely, but the shift of the LO phonon frequency in any zinc-blende semiconductor due to a strain of this magnitude would typically be no more than one or two wave numbers¹⁵ and would certainly not affect the identification of the Raman signals discussed here. Similarly, the small level of Zn incorporation in the MgS layers is not expected to modify the phonon frequencies significantly.

As a check of the consistency of the quantities calculated here, we can proceed as follows. The elastic constants can be used to estimate the LO phonon frequency following Harrison¹⁶ since, in a simple model, bond stretching and bond bending force constants C_0 and C_1 , respectively, can be defined as follows (a is the lattice parameter):

$$C_0 = (3a^3/16)(c_{11} + 2c_{12}), \quad (1)$$

$$C_1 = (a^3/32)(c_{11} - c_{12}). \quad (2)$$

The LO phonon frequency is then given approximately by the following expression, in which μ is the reduced mass of a MgS formula unit and d is the interatomic distance:

$$\omega_{\text{LO}}^2 = (8/3\mu d^2)(C_0 + 8C_1). \quad (3)$$

This procedure gives a value of 437 cm^{-1} , again in good agreement with the observed value.

The final observation is that the strength of the Raman scattering and the presence and sharpness of the several overtone bands strongly suggest that the excitation energy (5.08 eV) is close to the band gap energy and that the scattering is resonantly enhanced. This is reinforced by the undetectability of the MgS phonon Raman scattering when using below-band-gap excitation (2.95 eV). Similar observations have been made in many other semiconductor systems.¹⁷ The band gap of ZB MgS is not well known, with values ranging from an indirect gap of 3.7 eV (Ref. 18) to a direct gap of 5.9 eV (Ref. 19) being proposed. The most recent estimates, based generally either on extrapolation of the band gap of quaternary $\text{Zn}_{1-x}\text{Mg}_x\text{S}_{1-y}\text{Se}_y$ or on modeling of the optical spectra of heterostructures, are typically around 5.2–5.5 eV (Ref. 6) at low temperatures. Our observations do not provide a direct measurement of the band gap but do support a value of around 5.1 eV at room temperature and, assuming a shift with temperature similar to that of ZnS,⁷ lead to an estimated value of 5.4 eV at 5 K.

VI. CONCLUSIONS

The zone-center LO phonon frequency of zinc-blende MgS has been determined experimentally to be $425 \pm 1 \text{ cm}^{-1}$ (52.6 meV) and a tentative value of 327

$\pm 6 \text{ cm}^{-1}$ (40.5 meV) has been deduced for the zone-center TO phonon frequency. Both values are consistent with the results of first-principles calculations. The calculations also yield values for the lattice parameter and elastic constants that differ significantly from previously published results but are consistent with the present experimental results.

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- ¹H. Mutschke, B. Begemann, J. Dorschner, and T. Henning, *Infrared Phys. Technol.* **35**, 361 (1994).
²K. Uesugi, T. Obinata, I. Suemune, H. Kumano, and J. Nakahara, *Appl. Phys. Lett.* **68**, 844 (1996).
³L. Konczewicz, P. Biegenwald, T. Cloitre, M. Chibane, R. Ricou, P. Testud, O. Briot, and R.L. Aulombard, *J. Cryst. Growth* **159**, 117 (1996).
⁴L.D. Stockton, T.L. Ng, N. Maung, and A.C. Wright, *J. Mater. Sci.: Mater. Electron.* **9**, 207 (1998).
⁵N. Teraguchi, H. Mouri, Y. Tomomura, A. Suzuki, H. Taniguchi, J. Rorison, and G. Duggan, *Appl. Phys. Lett.* **67**, 2945 (1995).
⁶C. Bradford, C.B. O'Donnell, B. Urbaszek, A. Balocchi, C. Morhain, K.A. Prior, and B.C. Cavenett, *Appl. Phys. Lett.* **76**, 3929 (2000).
⁷*Numerical Data and Functional Relationships in Science and Technology*, edited by O. Madelung, Landolt-Börnstein, New Series, Group III, Vol. 22 (Springer-Verlag, Berlin, 1987).
⁸M.C. Payne, M.P. Teter, D.C. Allan, T.A. Arias, and J.D. Joannopoulos, *Rev. Mod. Phys.* **64**, 1045 (1992).
⁹D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
¹⁰H.J. Monkhorst and J.D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
¹¹T-Y. Chung, J.H. Oh, S-G. Lee, J-W. Jeong, and K.J. Chang, *Semicond. Sci. Technol.* **12**, 701 (1997).
¹²G. P. Srivastava, *The Physics of Phonons* (Adam Hilger, Bristol, 1990).
¹³K. Kunc and P. Gomes Dacosta, *Phys. Rev. B* **32**, 2010 (1985).
¹⁴N.B. Manson, W. von der Ohe, and S.L. Chodos, *Phys. Rev. B* **3**, 1968 (1971).
¹⁵S. Perkowitz, *Optical Characterization of Semiconductors* (Academic Press, London, 1993).
¹⁶W. A. Harrison, *Electronic Structure and the Properties of Solids* (W. H. Freeman, San Francisco, 1980).
¹⁷R. M. Martin and L. M. Falicov, in *Light Scattering in Solids I*, edited by M. Cardona (Springer-Verlag, Berlin, 1983).
¹⁸G. Kalpana, B. Palanivel, R.M. Thomas, and M. Rajagopalan, *Physica B* **222**, 223 (1996).
¹⁹S. Albin, J.D. Satira, D.L. Livingston, and T.A. Shull, *Jpn. J. Appl. Phys., Part 1* **31**, 715 (1992).