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Infrared and Raman study of lattice vibrations of CdAl₂Se₄ and CdAl₂S₄ single crystals

A Eifler†, J-D Hecht†, V Riede†, G Lippold†, W Schmitz‡, G Krauß§, V Krämer§ and W Grill†

† Institut für Experimentelle Physik II, Universität Leipzig, Linnéstraße 5, D-04103 Leipzig, Germany

‡ Institut für Mineralogie, Kristallographie und Materialwissenschaft, Universität Leipzig, Scharnhorststraße 20, D-04275 Leipzig, Germany

§ Freiburger Materialforschungszentrum, Albert-Ludwigs-Universität, Stefan-Meier-Straße 21, D-79104 Freiburg, Germany

E-mail: eifler@physik.uni-leipzig.de

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Abstract. Infrared and Raman spectra of oriented CdAl₂Se₄ single crystals and of as-grown CdAl₂S₄ single crystals have been measured in the wavenumber range from 600 to 25 cm⁻¹. Both ordered vacancy compounds grown by the chemical vapour transport method crystallize in the thiogallate structure with space group $I\bar{4}$. All 13 optical phonon modes are Raman active; ten of these are in addition infrared active. We report for the first time the combined infrared and Raman study of the optical phonon modes of both compounds. With the complementary information from infrared and Raman spectroscopy all optical phonon modes have been identified and assigned to their corresponding symmetry classes. The fact that all five modes of E symmetry exhibit a counterpart of B symmetry in the close spectral environment is unambiguous evidence of space group $I\bar{4}$. The measured frequencies of the nonpolar modes are in a very good agreement with data calculated in the framework of a simplified Keating model. For an oriented CdAl₂Se₄ single crystal the directional dispersion of the polar phonons has been studied.

1. Introduction

Since some of the chalcopyrites and related defective compounds exhibit very interesting physical properties with a high potential of technological applications most of them have been well investigated. While the A^{II}B₂^{III}C₄^{VI} ordered vacancy compounds with B^{III} = Ga or In are well studied due to complications with respect to crystal growth and sample preparation, such as the high oxygen affinity of aluminium, much less is known about the corresponding A^{II}Al₂C₄^{VI} compounds. Very recently the optical properties in the band gap region of CdAl₂Se₄ have been studied by optical spectroscopy [1], luminescence [2] and generalized ellipsometry [3]. Concerning the lattice vibrational properties, however, no experimental data are available. For CdAl₂S₄ investigations of the fundamental absorption as well as of the optical phonons have been reported [1, 4–10].

In this work we report the combined infrared and Raman study of oriented CdAl₂Se₄ single crystals and, in comparison, that of as-grown CdAl₂S₄ single crystals. Both isotypic compounds crystallize in the prototypic thiogallate structure (space group $I\bar{4}$) with two formula

units per unit cell [1, 11]. The irreducible representation of the optical phonon modes at the centre of the Brillouin zone is given by

$$\Gamma_{opt} = 3 A \otimes 5 B \otimes 5 E.$$

All modes are Raman active. In addition, the B and E modes are infrared active for $E \parallel c$ and $E \parallel a$ respectively [12]. For a general propagation direction in optically anisotropic media the coupled lattice–electromagnetic field equations are satisfied by ordinary and extraordinary waves. For space group $I\bar{4}$ the extraordinary waves correspond to TO + LO mixed character or B + E mixed symmetry phonons (the so called oblique phonons) exhibiting directional dispersion [13–16]. Therefore, the transverse or longitudinal character of the phonons or their symmetry classification does not apply in case of a propagation out of principal crystallographical directions. Care must be taken to avoid the frequency shift due to oblique phonon scattering in determining the principal phonon frequencies of the materials.

2. Experiment

The crystals were grown by the chemical vapour transport method [1]. CdAl_2Se_4 isometric crystals with a maximum edge-length of about 10 mm were obtained. Crystals were oriented and a (100) plane was cut and polished to allow far infrared reflectivity measurements with $E \parallel c$ and $E \parallel a$. To study the oblique phonon Raman scattering a sample was polished cylindrically with an a -axis as the main axis. This allowed us to vary the angle Θ between the c -axis of the crystal and the optical beam inside the crystal in the backscattering Raman measurements.

For CdAl_2S_4 thin crystals with a maximum size of about $15 \times 4 \times 1 \text{ mm}^3$ were obtained. The largest face of these crystals which was of optical quality and always of (112) orientation has been used for the infrared measurements. On this face reflectivity measurements with $E \perp c$ and $E \parallel c^*$, where c^* denotes the projection of the c -axis to the measured plane, were performed.

Polarized infrared reflectivity measurements at an angle of incidence of 11° and transmittance measurements were carried out at room temperature and at 10 K, respectively, in the wavenumber range from 600 to 35 cm^{-1} with a resolution of 0.5 cm^{-1} using a Bruker Fourier-transform spectrometer model IFS 113v. The transverse optical mode frequencies as well as the related oscillator strengths and damping constants were calculated by fitting the reflectivity spectra with a harmonic oscillator model. The longitudinal optical mode frequencies were obtained from the energy loss function calculated within the same fitting procedure.

With 514.5 nm laser excitation, Raman measurements in backscattering as well as in rectangular configurations were performed in the wavenumber range from 600 to 25 cm^{-1} at room temperature and at 10 K. The spectral resolution was set to 1.5 cm^{-1} . For the Raman measurements we used a Dilor XY 800 triple monochromator Raman spectrometer equipped with a liquid nitrogen cooled multichannel CCD detector. The wavenumber accuracy was controlled calibrating the spectra against the lines of a neon lamp. With the band gaps of $E_g = 2.95 \text{ eV}$ (CdAl_2Se_4) and $E_g = 3.82 \text{ eV}$ (CdAl_2S_4) at room temperature [1] the crystals are transparent for the 514.5 nm laser excitation.

3. Results

As predicted by group theory for space group $I\bar{4}$ the reflectivity spectra of CdAl_2Se_4 and CdAl_2S_4 showed five modes for both directions of polarization. For the oriented samples of

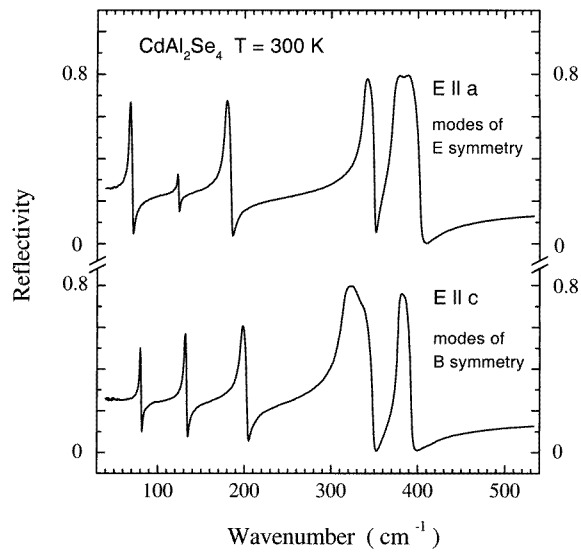


Figure 1. Infrared reflectivity spectra of CdAl_2Se_4 at room temperature with a resolution of 0.5 cm^{-1} .

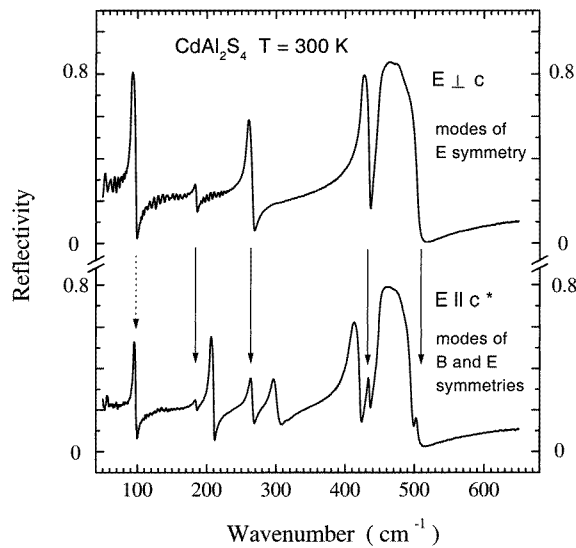


Figure 2. Infrared reflectivity spectra of the (112) face of CdAl_2S_4 at room temperature with a resolution of 0.5 cm^{-1} . Arrows indicate modes of E symmetry in the spectrum with polarization $E \parallel c^*$. At 95 cm^{-1} there are two modes, one of B symmetry and one of E symmetry.

CdAl_2Se_4 the features of the spectra are well separated. For both infrared active symmetries, B and E, two high frequency modes in the wavenumber range from 400 to 300 cm^{-1} and three modes at lower wavenumbers in the range from 200 to 70 cm^{-1} have been observed (figure 1).

The (112) face of the CdAl_2S_4 crystals showed the reflectivity spectra with polarizations $E \perp c$ and $E \parallel c^*$ as plotted in figure 2. As for selenide the reflectivity spectra of CdAl_2S_4 exhibit each two high frequency modes in the wavenumber range from 500 to 400 cm^{-1} and

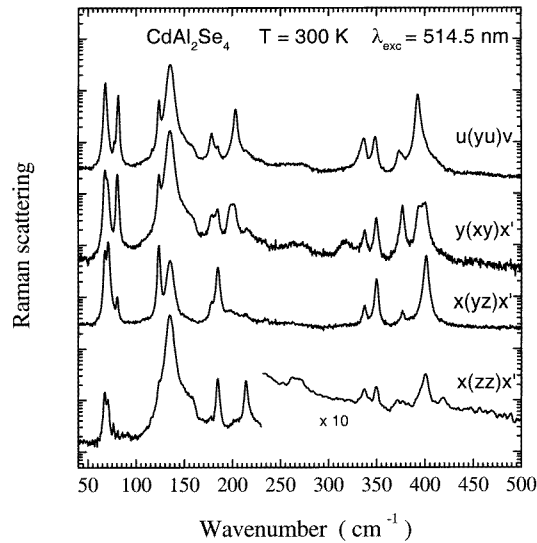


Figure 3. Raman spectra of CdAl_2Se_4 at room temperature with a resolution of 1.5 cm^{-1} . $x = [100]$, $y = [010]$, $z = [001]$, $x' = [100]$, $u = [\bar{1}01]$ and $v = [\bar{1}0\bar{1}]$.

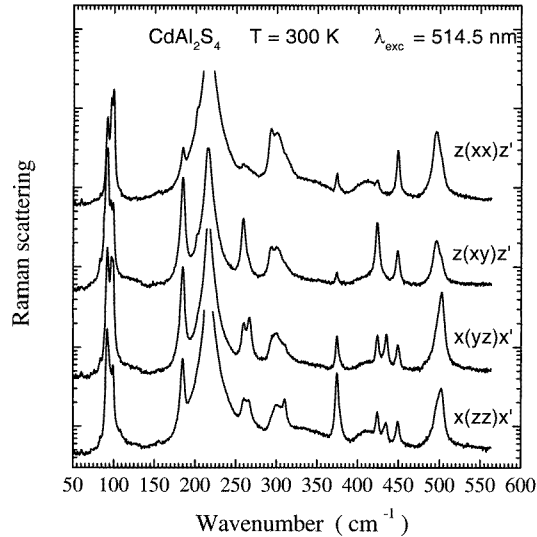


Figure 4. Raman spectra of CdAl_2S_4 at room temperature with a resolution of 1.5 cm^{-1} . $x = [100]$, $y = [010]$, $z = [001]$, $x' = [\bar{1}00]$, $z' = [00\bar{1}]$.

each three modes at lower wavenumbers in the range from 300 to 90 cm^{-1} for both infrared active symmetries. The Raman measurements confirmed the existence of two modes around 95 cm^{-1} , one of E symmetry and one of B symmetry. Thus, the spectra of CdAl_2Se_4 and CdAl_2S_4 can be compared very well.

An arbitrary plane cut from a uniaxial crystal always allows one to perform measurements with incident light polarized perpendicular to the c -axis of the crystal ($E \perp c$). In this case the vector of the electric field lies in the $a \otimes a$ plane and the measured reflectivity spectra

Table 1. Optical mode wavenumbers of CdAl₂Se₄.

Symmetry	$T = 300$ K (IR reflectivity and Raman)		$T = 10$ K (Raman only ^a)	
	$\bar{\nu}_{TO}$ (cm ⁻¹)	$\bar{\nu}_{LO}$ (cm ⁻¹)	$\bar{\nu}_{TO}$ (cm ⁻¹)	$\bar{\nu}_{LO}$ (cm ⁻¹)
E	67.5	71	69	72
B	80	81.5 ^b	82	[83]
E	123.5	124 ^b	124	[125]
B	131.5 ^b	133.5 ^b	[133]	[135]
A ^c	135.5		136.5	
E	178	185	181	186.5
A ^c	185		186.5	
B	197	203	201	204.5
A ^c	215		216.5	
B	315	348	317	—
E	338.5	350.5	342.5	353.5
E	373	402	377	405.5
B	377.5	392.5	381	—

The values of the infrared and Raman measurements differ only within the resolution limit of the Raman measurements which is about 1.5 cm⁻¹.

^a The assignment of the phonon frequencies was done in comparison with the room temperature measurements. Values given in square brackets were obtained exclusively from infrared transmittance measurements at 10 K where the low frequency modes show very sharp lines.

^b The TO–LO splitting was determined by the fit of the infrared reflectivity. The mode of B symmetry in the spectral vicinity of the high intensity mode of A symmetry was observed from the infrared reflectivity spectra only.

^c Raman active only.

From the fit of the infrared reflectivity the following values of the real part of the dielectric function were obtained:

$$\varepsilon_{\infty}(E \parallel a) = 5.51 \quad \varepsilon_0(E \parallel a) = 8.28 \quad \varepsilon_{\infty}(E \parallel c) = 5.36 \quad \varepsilon_0(E \parallel c) = 8.13.$$

are the same as with polarization $E \parallel a$ exhibiting modes of E symmetry. Measurements with polarization $E \parallel c$ require planes with an $(hk0)$ orientation, where h and k are Miller indices. Otherwise the plane contains only the projection c^* of the c -axis and the reflectivity spectra with polarization $E \parallel c^*$ exhibit both modes of B and E symmetries, due to a non-vanishing component of $E \parallel a$. In figure 2 the arrows indicate the influence of the component $E \parallel a$ on the reflectivity spectrum with polarization $E \parallel c^*$. In evaluating such a spectrum a more complex expression which allows to calculate the dielectric function for an arbitrary propagation direction has to be used in the fitting procedure [17]. But with a large number of phonons to be considered this calculation becomes uncertain. If the phonon wavenumbers of the modes of E symmetry have been found by the fit of the reflectivity spectrum with polarization $E \perp c$, the exact values of the phonon wavenumbers of the B symmetry modes can be obtained from the Raman spectra using the information about their spectral positions from the reflectivity spectrum with polarization $E \parallel c^*$ and excluding modes of E and A symmetries. Thereby the assignment of the A symmetry modes can be proved by the predictions of a theoretical model (see discussion).

Raman measurements were carried out in backscattering as well as in rectangular geometries. The Raman tensor and the phonon modes allowed at the different scattering geometries and polarizations for space group $I\bar{4}$ are given in [18] for example. The Raman spectra of both compounds are plotted in figures 3 and 4. The wavenumbers of the lattice vibrational modes of CdAl₂Se₄ and CdAl₂S₄ obtained from the fit of the infrared reflectivity at room temperature and from Raman spectroscopy at room temperature and at 10 K are given

Table 2. Optical mode wavenumbers of CdAl₂S₄.

Symmetry	$T = 300$ K (IR reflectivity and Raman ^a)		$T = 10$ K (Raman only ^b)		Literature data at $T = 300$ K	
	$\bar{\nu}_{TO}$ (cm ⁻¹)	$\bar{\nu}_{LO}$ (cm ⁻¹)	$\bar{\nu}_{TO}$ (cm ⁻¹)	$\bar{\nu}_{LO}$ (cm ⁻¹)	[8]	[6]
					$\bar{\nu}$ (cm ⁻¹)	$\bar{\nu}$ (cm ⁻¹)
E	91.5	98	92.5	[98]	91/94	—
B	95	[98]	95.5	[100.5]	98	94
E	183.5	185	—	185.5	184	184
			[183]	[185.5]		
B	203 shoulder		—	—	—	206
	[206.5]	[210.5]	[203.5]	[211]		
A ^c	215.5		217.5		216	
E	259	267	262.5	267	258	261
B	293	300.5	300.5	(300.5)	299	295
A ^c	310		—		307	
A ^c	374.5		376.5		374	
B	411	(424.5)	—	—	424	412
	[410.5]	[422]				
E	424.5	435.5	426.5	436.5	434	425
E	449.5	504	453	(504)	449/496	452
B	(449.5)	495.5	(453)	504	449/500	452
	[450.5]					

^a The phonon frequencies of the modes of E symmetry were obtained from the fit of the infrared reflectivity. In this case the values of the infrared and Raman measurements differ only within the resolution limit of the Raman measurements which is about 1.5 cm⁻¹.

The phonon frequencies of the modes of B symmetry were obtained from the Raman measurements. We report in parenthesis the values which can be assigned twice. The values given in square brackets were obtained from the fit of the infrared reflectivity which is disturbed by the mixing of modes of B and E symmetries.

^b The assignment of the phonon frequencies was done in comparison with the room temperature measurements. We report in parenthesis the values which can be assigned twice. The values given in square brackets were obtained from the infrared transmittance measurements at 10 K where the low frequency modes show very sharp lines.

^c Raman active only.

From the fit of the infrared reflectivity the following values of the real part of the dielectric function were obtained:

$$\varepsilon_{\infty}(E \parallel a) = 4.47 \quad \varepsilon_0(E \parallel a) = 7.87.$$

in tables 1 and 2, respectively. For CdAl₂S₄ the literature data are included. The calculated oscillator strengths and damping constants for both compounds are given in table 3.

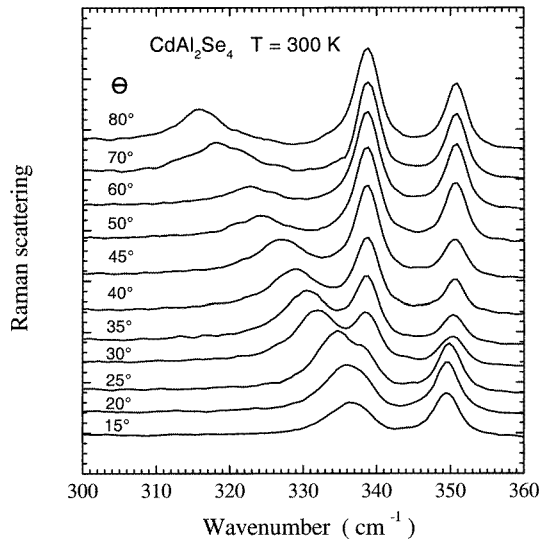
Even if the mode symmetry of some Raman lines leads to no activity in a given scattering geometry, they do not vanish completely in the corresponding spectra. This may be due to elastic light scattering inside the crystals or optical activity leading to a breakdown of the selection rules. All Raman lines could be identified in comparison with the infrared reflectivity spectra. For all polar modes of CdAl₂Se₄ and the E symmetry modes of CdAl₂S₄ the optical mode frequencies obtained from the fit of the infrared reflectivity spectra and from the Raman spectra agree very well.

Varying the angle Θ between the c -axis of the cylindrically polished CdAl₂Se₄ crystal and the optical beam inside the crystal in the backscattering Raman measurements the frequency dependence of the oblique phonons was studied. The strongest effect was observed in the spectral range between the B_{TO} phonon at 315 cm⁻¹ and the E_{TO} phonon at 338.5 cm⁻¹ (figure 5). This couple of phonons exhibits the largest frequency difference of neighbouring principal phonons of this material (which means phonons propagating along the crystallographical axes) which are the limiting cases of the oblique phonons. The frequency

Table 3. Oscillator strengths $\Delta\varepsilon_i$ and damping constants γ_i obtained from the fit of the infrared reflectivity of CdAl₂Se₄ and CdAl₂S₄.

Symmetry	CdAl ₂ Se ₄		CdAl ₂ S ₄	
	$\bar{\nu}_{TO}$ (cm ⁻¹), $\bar{\nu}_{LO}$ (cm ⁻¹)	$\Delta\varepsilon_i, \gamma_i$ (cm ⁻¹) ^a	$\bar{\nu}_{TO}$ (cm ⁻¹), $\bar{\nu}_{LO}$ (cm ⁻¹)	$\Delta\varepsilon_i, \gamma_i$ (cm ⁻¹) ^a
E	67.5, 71	0.790, 1.39	91.5, 98	1.051, 1.30
B	80, 81.5	0.263, 1.18	[95], [98]	[0.436], [2.12]
E	123.5, 124	0.085, 1.65	183.5, 185	0.090, 3.08
B	131.5, 133.5	0.317, 1.56	[206.5], [210.5]	[0.274], [2.36]
E	178, 185	0.592, 2.80	259, 267	0.424, 4.38
B	197, 203	0.549, 3.50	[297.5], [303]	[0.229], [8.32]
B	315, 348	1.432, 6.91	[410.5], [422]	[0.564], [6.52]
E	338.5, 350.5	0.734, 3.26	424.5, 435.5	0.777, 3.60
E	373, 402	0.575, 4.09	449.5, 504	0.678, 7.10
B	377.5, 392.5	0.208, 2.48	[450.5], [495.5]	[0.615], [8.10]

^a Using $\varepsilon(\bar{\nu}) = \varepsilon_\infty + \sum (\Delta\varepsilon_i \bar{\nu}_{TO,i}^2) / (\bar{\nu}_{TO,i}^2 - \bar{\nu}^2 - i\gamma_i \bar{\nu})$ for each direction of polarization. Comparing the data with values given in [17] for example, note the relation $\Delta\varepsilon_i = 4\pi\rho_i$.

**Figure 5.** Oblique phonon Raman scattering of CdAl₂Se₄ at room temperature. Theta is the angle between the *c*-axis of the crystal and the optical beam inside the crystal in the backscattering Raman measurements.

dependence of this TO character B + E symmetry mixed phonon with respect to the phonon propagation direction, given by equation (1) [16], is plotted in figure 6.

$$\bar{\nu}^2 = \bar{\nu}_{B_{TO}}^2 \sin^2 \Theta + \bar{\nu}_{E_{TO}}^2 \cos^2 \Theta. \quad (1)$$

$\bar{\nu}$ denotes the phonon wavenumber. The circles in figure 6 indicate the calculated frequencies of this phonon for the spectra which are shown in figure 5. The measured phonon frequencies agree with this calculation within the experimental error limit. In contrast to the oblique phonon which corresponds to the extraordinary wave the frequency of the E_{TO} phonon (338.5 cm⁻¹) corresponding to the ordinary wave is unshifted. For the oblique LO phonon only a small shift between the frequencies of the principal phonons is observable. This is similar to the other oblique phonon modes exhibiting low dispersion.

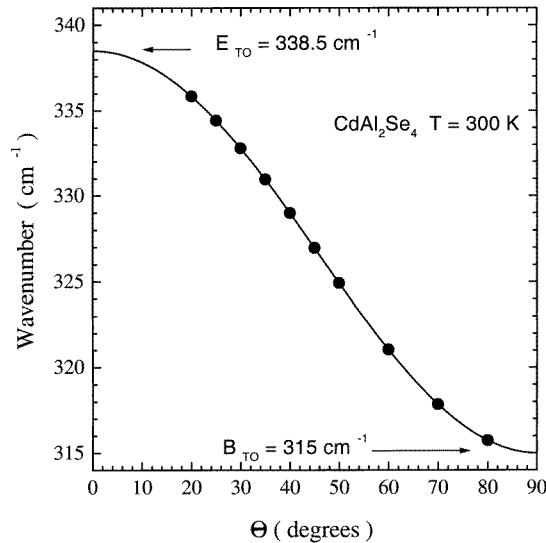


Figure 6. Frequency dependence of the TO phonon of B + E mixed symmetry with respect to the phonon propagation direction. Circles indicate the calculated frequencies for the spectra shown in figure 5.

The phonon frequencies of both compounds measured at 10 K were only weakly shifted to higher frequencies compared with those measured at room temperature (tables 1 and 2). No shift to lower frequencies indicating a soft mode behaviour was observed. These findings are in accordance with Raman investigations of CdAl₂S₄ [7] and CdGa₂S₄ [19] at room temperature and at 77 K. To our knowledge, no other investigations of the lattice vibrational properties of the A^{II}B₂^{III}C₄^{VI} defect chalcopyrite compounds at low temperatures have been reported so far.

For CdAl₂Se₄ four lines of the Raman spectra have been assigned to multiphonon scattering processes. These Raman lines and a possible assignment are given in table 4. The combinations of two modes of the symmetries of space group $I\bar{4}$, A, B or E, lead to Raman tensors which allow scattering within the geometries used in this study.

4. Discussion

We report the optical mode frequencies of CdAl₂Se₄ for the first time. Infrared and Raman measurements yielded the data given in table 1 in a very good agreement. The assignment of the modes to the symmetry classes B and E is demonstrated by the infrared measurements in a consistent way. The remaining three modes of A symmetry were found in the Raman spectra only. The fact that all five modes of E symmetry exhibit a counterpart of B symmetry in the close spectral environment is unambiguous evidence for space group $I\bar{4}$. In the infrared reflectivity spectra of the gallium compounds, strongly assumed to crystallize in space group $I\bar{4}$, reported by Haeuseler *et al* [17] and Nikolic and Stojilkovic [20] the counterparts of the modes of lowest frequencies are missing. From the Raman scattering investigations of the A^{II}B₂^{III}C₄^{VI} compound family by Razzetti and Lottici [8] and from calculations reported by Ohrendorf and Haeuseler [21] it is obvious, however, that for space group $I\bar{4}$ each mode of E symmetry is closely accompanied by a mode of B symmetry, and *vice versa*.

Table 4. Multiphonon Raman scattering in CdAl₂Se₄.

Raman line (cm ⁻¹)	Assignment
160	2 B _{TO} (80 cm ⁻¹)
264	2 B _{TO} (131.5 cm ⁻¹)
270	2 A (135.5 cm ⁻¹)
417	A (215 cm ⁻¹) + B _{LO} (203 cm ⁻¹)

Haeuseler and Cansiz [6] reported infrared absorbance measurements of CdAl₂S₄ powder for the first time. The lines they observed (see table 2) correspond within the error limit to the frequencies of the infrared active B_{TO} and E_{TO} modes found in our study. First Raman measurements [4, 10] demonstrated the existence of one B and one E symmetry modes at wavenumbers at 91, 93.5 and 98 cm⁻¹. A first comparison of infrared reflectivity and Raman measurements of CdAl₂S₄ showed still some contrary data [7]. A more comprehensive set of Raman data is given by Razzetti and Lottici [8] (see table 2) who compared the Raman scattering of the A^{II}B₂^{III}C₄^{VI} compounds. Within the error limits, similar data were reported recently in a Raman scattering study of CdAl₂S₄ under hydrostatic pressure [9].

With the complementary information from infrared and Raman spectroscopy our study leads to the following results for CdAl₂S₄: (i) there are two modes at low frequencies, one of E symmetry (91.5 cm⁻¹/98 cm⁻¹) and one of B symmetry (95 cm⁻¹/98 cm⁻¹) with the same LO frequencies. (ii) The B symmetry mode of second lowest frequency was confirmed at wavenumbers around 205 cm⁻¹. (iii) The phonon frequencies of the high frequency polar modes could be separated. The TO frequencies of the highest and second highest modes exhibit a B–E–B sequence, whereas the LO frequencies exhibit a B–E–B–E sequence (see table 2). This means that the high frequency mode of E symmetry covers the spectral range of that of B symmetry. This is also valid for CdAl₂Se₄ in contrast to the related gallium compounds [8, 17]. The fact that E_{LO} > B_{LO} for the modes of highest frequencies of CdAl₂S₄ is demonstrated in figure 2 which shows the influence of the modes of E symmetry to the spectrum with polarization E || c*. In this way, the presented data complete the knowledge of the lattice vibrational properties of CdAl₂S₄.

Comparing the oscillator strengths (table 3) with values of the related gallium compounds given in [17] no simple trends can be observed. In general, the E symmetry mode of second lowest frequency exhibits a very low oscillator strength which is nearly constant in all compounds. Also the B symmetry mode of lowest frequency seems to be very weak in the gallium compounds. For a detailed discussion concerning oscillator strengths and damping constants most of the data are assumed to be too much affected by depolarization or coupling of modes with different symmetries.

To obtain more insight we will now discuss some selected modes within the A^{II}B₂^{III}C₄^{VI} compounds. Neumann has analysed the lattice vibrations and interatomic forces in A^{II}B₂^{III}C₄^{VI} defect-chalcopyrite compounds [22, 23]. From Keating model considerations analytical expressions are given for the nonpolar A modes and the high frequency polar modes of B and E symmetries. Following the common notation the modes are now marked with an upper index which increases with descending mode frequency. The expressions given by Neumann are

$$\omega^2(A^1) = 4\alpha_{B0}/m_C \quad (2)$$

$$\omega^2(A^2) = (\alpha_{A0} + \alpha_{V0} + 2\alpha_{B0})/m_C \quad (3)$$

$$\omega^2(A^3) = 2(\alpha_{A0} + \alpha_{V0})/m_C \quad (4)$$

$$\omega^2(B^1, E^1) = 4\alpha_B(1/m_B + 1/m_C) \quad (5)$$

Table 5. Bond lengths, calculated force constants and calculated as well as experimentally determined wavenumbers of the nonpolar modes.

	CdAl ₂ Se ₄	CdAl ₂ S ₄	CdGa ₂ Se ₄	CdGa ₂ S ₄
B ^{III} -C ^{VI} bond length d_B (nm)	0.2402 ^a	0.2252 ^a	0.2424 ^a	0.2278 ^a
	0.2391 ^b (Al ₁)	0.2243 ^b (Al ₁)		
	0.2386 ^c (Al ₂)	0.2193 ^c (Al ₂)		
Force constant α_{B0} from equation (6) (N m ⁻¹)	52.49 ^a	62.05 ^a	51.21 ^a	60.28 ^a
	53.13 ^b	62.68 ^b		
	53.43 ^c	66.27 ^c		
Calculated wavenumber $\bar{\nu}$ (A ¹) from equation (2) (cm ⁻¹)	212 ^a	363 ^a	210 ^a	358 ^a
	214 ^{b,c}	365 ^b		
		375 ^c		
Measured wavenumber $\bar{\nu}$ (A ¹) (cm ⁻¹)	215 ^e	374.5 ^e	207 ^f	360 ^f
A ^{II} -C ^{VI} bond length d_A (nm)	0.2630 ^a	0.2532 ^a	0.2575 ^a	0.2532 ^a
	0.2624 ^d	0.2556 ^d		
Force constant $\alpha_{A0} + \alpha_{V0}$ from equation (7) (N m ⁻¹)	42.53 ^a	45.14 ^a	43.98 ^a	45.14 ^a
	42.68 ^d	44.49 ^d		
Calculated wavenumber $\bar{\nu}$ (A ³) from equation (4) (cm ⁻¹)	135 ^a	219 ^a	138 ^a	219 ^a
	135 ^d	217 ^d		
Measured wavenumber $\bar{\nu}$ (A ³) (cm ⁻¹)	135.5 ^e	215.5 ^e	138 ^f	218 ^f
Calculated wavenumber $\bar{\nu}$ (A ²) from equation (3) (cm ⁻¹)	178 ^a	300 ^a	178 ^a	298 ^a
	179 ^{b,c}	300 ^b		
		306 ^c		
Measured wavenumber $\bar{\nu}$ (A ²) (cm ⁻¹)	185 ^e	310 ^e	184 ^f	310 ^f

^a Values as used in [23].

^{b-d} Bond lengths for the three different positions of the cations from [1] and calculated values using these bond lengths.

^e This work.

^f From [8].

where ω is the circular frequency, α_i are force constants ($i = A0, B0, V0$ for the nonpolar modes and $i = A, B, V$ for the polar modes) and the m_j are the atomic masses ($j = A, B, C$) [22].

In deriving (2) to (5) some approximations were made. At first all bond-bending force constants were neglected. In consequence, the modes of B and E symmetries are degenerate. Secondly, the bond-stretching force constants of the two different B^{III}-C^{VI} bonds were assumed to be equal. Finally, the contribution of Coulomb forces which were not included explicitly in calculating the dynamical matrix requires different sets of bond-stretching force constants for the nonpolar and polar modes, respectively. In this notation we have α_{B0} and α_B valid for the B^{III}-C^{VI} bond for nonpolar and polar modes, respectively, α_{A0} and α_A valid for the A^{II}-C^{VI} bond and α_{V0} and α_V in case of the fictive vacancy-C^{VI} bond describing the presence of the anion lone pair electrons. The force constants α_A and α_V and the masses m_A and m_B are necessary to calculate the frequencies of the remaining polar modes B²-B⁵ and E²-E⁵ which will not be discussed here [22].

Studying the lattice vibrational properties of the A^{II}B₂^{III}C₄^{VI} as well as of the A^IB^{III}C₂^{VI} compounds Neumann has found the following relations describing the dependence of the force constants of the nonpolar modes on the different bond lengths [23]

$$\alpha_{B0} = a_B \exp(-b_B d_B) \quad (6)$$

$$\alpha_{A0} + \alpha_{V0} = a_{AV} \exp(-b_{AV} d_A) \quad (7)$$

Table 6. Force constants calculated from the high frequency polar modes.

	CdAl ₂ Se ₄ ^a	CdAl ₂ S ₄ ^a	CdGa ₂ Se ₄	CdGa ₂ S ₄
$\bar{\nu} (E_{TO}^1) (\text{cm}^{-1})$	373	449.5	259 ^b 253 ^c	364 ^b 363 ^c
$\bar{\nu} (B_{TO}^1) (\text{cm}^{-1})$	377.5	450.5	261 ^b 259 ^c	371 ^b 366 ^c
Averaged $\bar{\nu} (E_{TO}^1, B_{TO}^1)$ used for the calculation (cm^{-1})	375	450	260 ^b 256 ^c	367 ^b 364.5 ^c
α_B from equation (5) (N m^{-1})	41.7	43.7	36.9 ^b 35.8 ^c	43.6 ^b 43.0 ^c
α_{B0} taken from table 5 with best agreement to the experimental data (N m^{-1})	53.4	66.3	51.2	60.3

^a This work.^b Phonon frequencies from [8].^c Phonon frequencies from [17].

with the constants $a_B = 766 \text{ N m}^{-1}$, $b_B = 1.116 \times 10^{10} \text{ m}^{-1}$, $a_{AV} = 211 \text{ N m}^{-1}$ and $b_{AV} = 6.09 \times 10^9 \text{ m}^{-1}$. d_B and d_A denote the length of the B^{III}-C^{VI} bond and of the A^{II}-C^{VI} bond, respectively. In table 5 the experimental and calculated data of the nonpolar modes of CdAl₂Se₄ and CdAl₂S₄ as well as of CdGa₂Se₄ and CdGa₂S₄ as related compounds are summarized. The calculated and measured wavenumbers are in a very good agreement. The wavenumbers calculated for CdAl₂S₄ showed the best agreement to the experimental values if $d_B = 0.2193 \text{ nm}$ valid for the nearest Al-S bond as given by Krauß [1] is used.

Only in the case of the A² modes is there a larger difference between the calculated and measured wavenumbers. Equations (2) to (4) contain only two parameters, α_{B0} and the sum $\alpha_{A0} + \alpha_{V0}$. Therefore the frequency of one of the three A modes is determined by the frequencies of the two others. Thus, if the frequencies of the A¹ and A³ modes agree very well, the difference between the calculated and measured frequencies of the A² mode indicate the limitations of the used model.

Finally, using equation (5) we have calculated the force constants α_B from the high frequency polar modes. In table 6 the force constants α_B are summarized and compared with the related force constants α_{B0} of the nonpolar modes. The trend of α_{B0} , following the bond length d_B as expressed by equation (6), is confirmed by the measurements (see table 5). The force constant α_B for the polar modes takes into account the contribution of Coulomb forces on the vibrational properties of the compounds but also follows the trend of α_{B0} .

5. Summary

In the present work we have reported the optical mode frequencies of oriented CdAl₂Se₄ single crystals and of as-grown CdAl₂S₄ single crystals using the complementary information from infrared and Raman spectroscopy. We have presented the data of CdAl₂Se₄ for the first time and completed the data already known for CdAl₂S₄. This opens up some new reflections on the lattice vibrational properties of the A^{II}B₂^{III}C₄^{VI} defect-chalcopyrites. Comparing the experimental data with theoretical considerations we observed a very good agreement between measured and calculated data for the nonpolar modes of CdAl₂Se₄ and CdAl₂S₄. Varying the angle Θ between the *c*-axis of the crystal and the phonon propagation direction we have observed the oblique phonon Raman scattering of CdAl₂Se₄.

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