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PHONON SPECTROSCOPY OF THE LOW ENERGY VIBRATIONS OF INTERSTITIAL OXYGEN IN GERMANIUM

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In oxygen doped Ge we find by phonon spectroscopy with superconducting tunnelling junctions a series of lines between 0.18 meV and 4.08 meV which can be interpreted as due to low lying states of the interstitial oxygen (O_i) as a rigid rotator around a <111>-axis slightly perturbed by the lattice potential. The sequence of transitions can be fit assuming a binding angle of $(106 \pm 1)°$ which is much smaller than the value of $(162 \pm 1)°$ for O_i in Si. Line shifts and splittings with uniaxial stress along <100>, <110>, and <111> are in qualitative agreement with this interpretation.

1. Introduction

The complex dynamics of interstitial oxygen (O_i) in Si and Ge is manifest from the observation of various series of infrared transitions[1,2,3,4] which can be related to vibrations of a bent molecule X_2O made up of O_i being squeezed in between nearest neighbours X in the [111]-direction of the diamond lattice. Such a triatomic molecule has three normal vibrations: the symmetric stretching ν_1, the symmetric bending ν_2, and the antisymmetric stretching ν_3. These modes will be modified by the surrounding lattice. Especially the details of the ν_2 - band, the lowest in energy, depend sensitively on the microscopic parameters such as the height of an axial barrier against inversion or the angular modulation of the potential due to the nearest lattice atoms.

In Si the ν_2-band lies in the FIR-range with levels at 3.62 meV, 8.32 meV, 9.72 meV, 13.69 meV, and 14.93 meV above the ground state. This band has been analysed in terms of a two-dimensional harmonic oscillator perturbed by the axial barrier[2,5,6] or, alternatively, in terms of a non-rigid rotator[2]. In both cases the analysis of the observed sequence of transitions leads to a quasilinear Si_2O-molecule with a binding angle $Si - O - Si$ of 162°, which was also estimated from a total energy calculation for O in a Si_8H_{18}-cluster[7].

In germanium to our knowledge analogous calculations of the oxygen position and the energy levels do not exist. From isotopic shifts of IR transitions corresponding to the antisymmetric mode ν_3 Pajot and Clauws[3] estimate an angle of about 140°. Using the approximation of a rigid rotator Khirunenko et al.[4] estimated with this angle the first excited level to be at about 0.4 meV above the ground state.

To obtain spectral information on such low lying modes phonon spectroscopy with superconducting tunnelling junctions[8] is an appropriate method. Its high resolution and sensitivity is apparent from previous investigations e.g. of the lattice coupling of the 3.62 meV O_i-resonance in silicon and in particular of the mutual shifts of this resonance of the few close O_i pairs at higher O_i concentrations[9]. In the following we report on the detection by this technique of low lying resonance states in Ge:O and their variation with [111], [110], and [100] uniaxial stress showing quantitative and qualitative differences to Si:O.

2. Experimental

As described e.g. in [8] superconducting tunnelling junctions may be used as phonon detectors with a detecting threshold given by the superconductor energy gap ($2\Delta_{Al} \geq 0.25$ meV, $2\Delta_{Sn} = 1.18$ meV) whereas for phonon generation Sn-junctions are suitable up to $2\Delta_{Sn} = 1.18$ meV and Al-junctions up to at least 14 meV[10] with a resolution of ≈ 30 μeV and ≈ 3 μeV, respectively. The superconducting tunnelling junction as a phonon generator produces a continuous spectrum up to a limiting frequency as determined by the junction bias. This limiting frequency is emphasized as a quasimonochromatic phonon line by modulation techniques. A small 'precursor' larger in energy by $2\Delta_{Al}$ than the main line comes from tunneling of thermally excited quasiparticles[8] (Cf. caption of Fig. 1). In some cases the continuous part of the phonon spectrum may be relevant in generating a nonequilibrium situation for the occupation of low lying levels[11]. The contribution of longitudinal phonons to the emitted spectrum can generally be neglected in comparison with that of the emitted transverse phonons[8]. Time of flight measurements are necessary to sort out the contribution of different polarizations.

Uniaxial stress was applied to the samples up to about 200 MPa by pulling a yoke assembly from top of the cryostat and was measured by either a piezoelectric cell immediate to the sample or a bridge of strain gauges glued to a structure in line with the pulling rod.

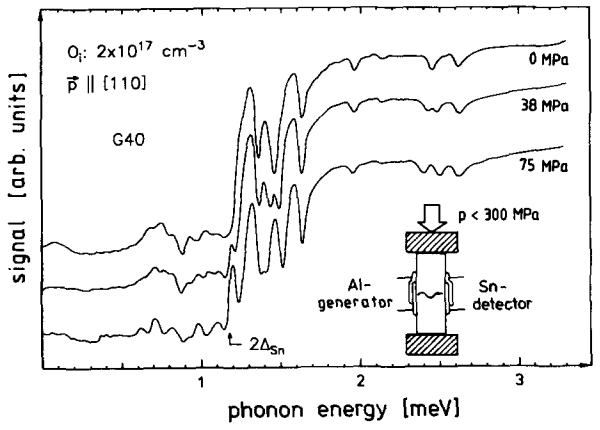

Figure 1: Detector signal versus energy of the quasimonochromatic phonon line of the sample G40 for three different stresses $\vec{p}$ || [110] at 1.0 K for the combination Al-generator ⇒ Sn-detector in the energy range above the sensitivity threshold of the Sn-detector at ≈ 1.2 meV. Isotope scattering is so effective in Ge that above ≈ 3.2 meV absorption minima could be observed only in a much thinner sample(G40th). The wiggles below the detector threshold are images of the absorption lines within a small precursor in the emission spectrum 'in front' of the quasimonochromatic line.

The uncertainty in the stress was less than 8 %. The working temperature could be varied from 0.4 K up to 1.4 K, the T_c of the superconducting Al-films.

Details of our samples are given in Table 1. The O_i concentration was determined from FIR absorption of the ν_3-band[12]. n-type conductivity at room temperature was taken as a measure of the concentration of thermal donors (TD) which can be produced by appropriate heat treatment in Ge:O as in Si:O. Typical dimensions for the samples were 2 × 5 × 15 mm^3 with a generator-detector distance of 2 mm.

Table 1: Concentration of interstitial oxygen ([O_i]: FIR absorption of the 855 cm^{-1}-band) and of the thermal donors ([TD]: room temperature conductivity) in the available samples. Also given is the orientation of the stress axis.

	O_i [cm^{-3}]	TD [cm^{-3}]	stress axis
G40th	$2.0 \cdot 10^{17}$	$< 1 \cdot 10^{14}$	(300μm)
G40 [a]	$2.0 \cdot 10^{17}$	$< 1 \cdot 10^{14}$	[110]
G45a [b]	$2.5 \cdot 10^{17}$	$6 \cdot 10^{15}$	[100]
G45b [b]	$2.2 \cdot 10^{17}$	$2.5 \cdot 10^{14}$	[100]
G45c [b]	$2.0 \cdot 10^{17}$	$3 \cdot 10^{15}$	[111]
G45f [b]	$\approx 5 \cdot 10^{15}$	$< 10^{14}$	[110]
G41 [c]	$5 \cdot 10^{17}$	$4 \cdot 10^{16}$	[110]

[a] This sample was prepared by P. Clauws, Rijksuniversiteit Gent, to have a minimum TDs with O_i concentration characterised by FIR. We have used his datum as a reference for our FIR measurements of the other samples.

[b] These CZ-grown samples were obtained from W. Kaiser, Techn. Univ., Munich (see e. g. Ref.[1]).

[c] This sample was obtained from V. V. Emtsev, Ioffe Institute, St. Petersburg.

3. Results

An example of phonon transmission characteristics for Al ⇒ Sn generator ⇒ detector set up is shown in Fig.1. Beyond the Al- and Sn-detector thresholds a series of phonon scattering minima is seen part of which split under stress. Higher energies than ≈ 3.2 meV were not measureable in the 2 mm thick samples due to the rapidly decreasing mean free path of the phonons in Ge by isotope scattering. In the thin sample G40th (0.3 mm, non-stressed) we find further lines at 3.90 and 4.08 meV. The linewidth is about 40 μeV and does not depend on the transition energy.

Correlated with the thermal donor concentration in the as received samples we observe a broad phonon absorbance below about 2.2 meV (Fig.2) which vanishes if the oxygen is dispersed by annealing and quenching.

Fig.3 shows the stress dependence of all the lines for uniaxial stress along [111], [110], and [100]. The lines at 0.49 meV, 1.19 meV, 1.47 meV, and 2.48 meV split nearly symmetrically in energy for stress $\vec{p}$ || [110] and $\vec{p}$ || [100], whereas for $\vec{p}$ || [111] only a small splitting within the magnitude of the linewidth was observed. 0.18 meV above each of these stress-doublets there is a non-splitting line at 0.67 meV, 1.37 meV, 1.65 meV, and 2.66 meV, respectively, with a nonlinear stress dependence strongest for [100]-stress. The two lines lowest in energy can be observed only for [100]-stress above 70 MPa and 110 MPa when they are shifting over the threshold of the Al-detector (≥ 0.25 meV depending on film parameters and working temperature). The stress

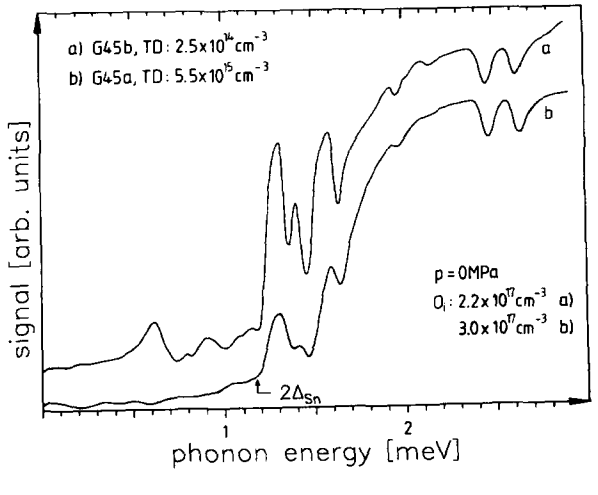

Figure 2: Comparison of transmission spectra for lower (a) and higher (b) TD-concentration. The broad absorbance below ≈ 2.2 meV is observed for all samples with higher TD-concentration.

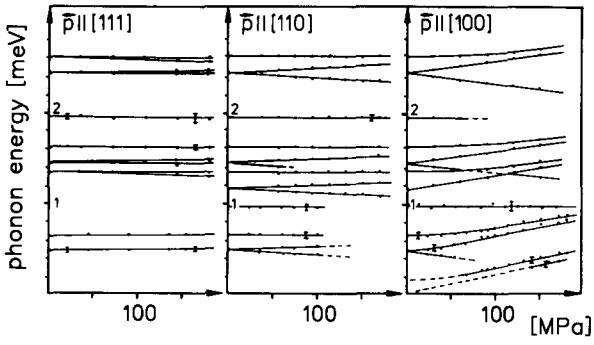

Figure 3: Stress dependence of the observed phonon transition energies of O_i in Ge for uniaxial stress along [111], [110], and [100]. The uncertainty of stress is less than 8%. For the line at 1.65 meV and $\vec{p} \parallel [111]$ only the indicated broadening could be measured. Unless otherwise indicated the error bars correspond to the size of the data points. Due to a misorientation of the [111]-sample by 3° there is a slight upward shift with stress of the lines at 0.49 meV, 1.47 meV, and 2.48 meV arising from a slight splitting of the 0.18 meV state in the proposed level scheme of Fig.4. The line at 0.98 meV could only be measured in the samples G40 and G45b with small TD-concentrations.

dependence of these two lines is twice as large as the stress dependence of the other lines. Note that the two additional lines at higher energies observed in the thin sample G40th have also a separation of 0.18 meV[13].

The depth of the line at 1.99 meV increases like $\exp\{(-0.66 \pm 0.04)\text{meV}/kT\}$ which suggests that this transition starts from a state at 0.67 meV. Similarly a temperature dependence of the depth of the stress split doublet at 1.47 meV is indicative that the doublets result from transitions from a state 0.18 meV above the ground state.

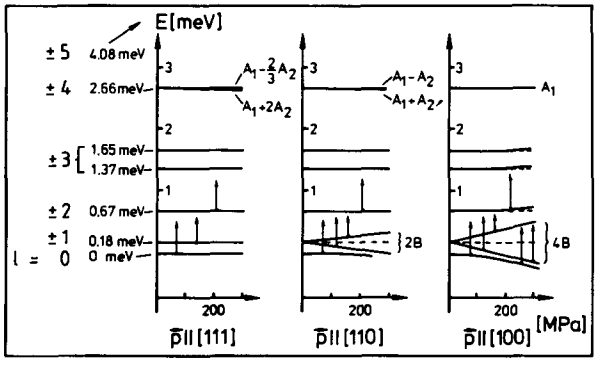

Figure 4: Proposed level scheme and stress dependence of the ν_2-band of O_i in Ge. Phonon induced transitions from the ground state and the first and second excited states have to be included to explain the observed resonances of Figure 3. The main stress dependence is due to a splitting of the state at 0.18 meV.

With these temperature dependences taken into account the measured lines can be interpreted as transitions in the level scheme shown in Fig. 4 with states 0.18 meV, 0.67 meV, 1.37 meV, 1.65 meV, 2.66 meV, and 4.08 meV above the ground state. Thus all the stress split doublets are interpreted as transitions from the first excited state at 0.18 meV split by stress and the lines at 0.98 meV and 1.99 meV as transitions from the second excited state at 0.67 meV.

For an estimate of relative transition probabilities the phonon mean free path should be larger than the sample thickness to have a linear relation between the line depth and the mean free path. For the sample with lowest oxygen concentration of $5 \cdot 10^{15}\text{cm}^{-3}$ we find (Fig.5), that the transition probability from the ground state to the level at 1.65 meV is smaller by a factor of 60 ± 15 than that from the level at 0.18 meV whereas the corresponding transitions to the level at 2.66 meV differ only by a factor of 2.1 ± 0.4.

4. Discussion

Obviously the spectra and the stress dependence of the low energy phonon transitions we observe for O_i in Ge are quite different from those observed for O_i in Si. These differences can be understood as a consequence of a much smaller binding angle of the Ge_2O-molecule i. e. a larger distance of O_i from the axis and therefore a stronger central potential barrier. The low-lying states may then be approximated by those of a rigid rotator with energy levels at[14]

$$E_l = [\hbar^2 / 2 \cdot \mu \cdot r_0^2] \cdot l^2 \qquad (l = 0, \pm 1, \pm 2, ...)$$

where μ is the reduced mass of Ge_2O and r_0 its distance from the rotational axis. The level scheme of Fig. 4 can

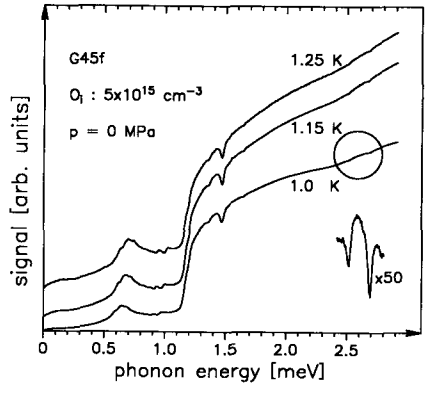

Figure 5: Transmission spectra at three temperatures of sample G45f with lower O_i content, i.e. without instrumental saturation of the lines. A weak temperature dependence of the strongest line at 1.47 meV is compatible with the level at 0.18 meV as the starting level of this transition.The inset shows the higher energy transitions with higher sensitivity.

be fitted by such a law if one assumes that the levels at 1.37 meV and at 1.65 meV result from the state $l = \pm 3$ split by a 6-fold angular perturbation. Such a potential is expected from the six lattice neighbours next-nearest to an O_i and has been invoked previously[14] in an attempt to fit the ν_2-level scheme in Si. To first order the measured splitting of 0.28 meV is equal to the amplitude of a sinusoidal potential modulation. Thus, in contrast to the case of Si there is a distinct influence of the surrounding lattice on the states in the ν_2-band. This is also consistent with the stress splitting of the $l = \pm 1$ state by the additional (interaction-)potential of twofold rotational symmetry. For Si:O_i a corresponding splitting of the first excited state has not been observed. (We are grateful to H. Yamada-Kaneta for pointing out to us the aspect of a slightly perturbed rigid rotator which was not specifically discussed in[14].) With (0.169 ± 0.006) meV as fitting prefactor in the above formula we get ≈ 0.17; 0.68; 1.52; 2.70; 4.23 meV for the $|l| = 1$; 2; 3; 4; 5 excited rotational states, respectively.

From the fitting prefactor above we obtain $r_0 = (93 \pm 2)$ pm i.e. a binding angle of $(106 \pm 1)°$ which is much smaller than the value of 140° obtained by Pajot and Clauws[3] in a different way. The observed splittings and line shifts can be described within the scheme given in[15,16] for the stress dependence of trigonal centers in cubic crystals (Table 2). There are two piezospectroscopic constants A_1 and A_2 related to the shift of the resonance under axial stress of a center which leads to a partial lifting of the fourfold orientational degeneracy corresponding to the four <111> directions. Two constants B and C describe the splitting of the $l = \pm 1$ state. A_1 and A_2 should be proportional to the transition energy with the assumption of rigid Ge-O distances[2]. We obtain the following values for these piezospectroscopic parameters: $A_1 = A_2 = (-0.079 \pm 0.02)$ meV/GPa (for the 2.66 meV transition) and $A_1 = A_2 = (-0.059 \pm 0.02)$ meV/GPa (for the 1.65 meV transition), $B = (0.55 \pm 0.05)$ meV/GPa and $C = (0.00 \pm 0.02)$ meV/GPa. At higher stresses ($\vec{p} \parallel [110]$:> 100 MPa; $\vec{p} \parallel [100]$:> 50 MPa) the stress shifts become nonlinear due to a repulsion of the $l = 0$ state by the stress split $|l| = 1$ state.

Table 2: Stress dependent shifts of transition energies for trigonal centres with D_{3d} symmetry in the notation of Hughes and Runciman[16] between levels with the irreducible representation A_1 and E_1. The coefficients may be different for the transitions between the various levels. The coefficients A_1 and A_2 describe the shift of the rotational states under <111>-axial stresses lifting the orientational degeneracy, B and C describe the splitting of E_1.

uniaxial stress along	orientational degeneracy	splitting of E_1-states
[100]	A_1	$-2B$
	A_1	$+2B$
[111]	$A_1 + 2A_2$	
	$A_1 - \frac{2}{3}A_2$	$-\frac{4}{3}C$
	$A_1 - \frac{2}{3}A_2$	$+\frac{4}{3}C$
[110]	$A_1 + A_2$	$+C - B$
	$A_1 + A_2$	$-C + B$
	$A_1 - A_2$	$+C + B$
	$A_1 - A_2$	$-C - B$

Following Bosomworth et al.[2] who calculated the change in the momentum of inertia due to the additional outshift of the oxygen we can estimate A_1 and A_2 from the binding angle and the elastic constants. This estimate implies the assumptions that the Ge-O bond length is not changed in bending and that the local axial compression is given by the elastic constants. The values we obtained are too large by about a factor of 4. This may indicate that one or both of the above assumptions are not valid.

For all the transitions we observe the same linewidth of 40 μeV. From a rough estimate within the rigid rotator model the Ge isotopic broadening should contribute about 25 μeV to the linewidth. High resolution experiments with isotopically enriched Ge could then render additional information on the lattice contribution to the O_i rotation in Ge. Such a material would have the additional advantage of low isotopic scattering making perhaps possible the access to the $l = \pm 6$ state expected to be at ≈ 6 meV.

The broad absorbance below ≈ 2.2 meV correlated with thermal donors in the as received samples is unexplained as yet. FIR absorption measurements[17] indicate a multiplet structure of at least some of the TDs with well defined energy differences in this energy range which should be resolvable in our experiment. A band at 785 cm^{-1} correlated with the thermal donor concentration has been attributed to vibrational transitions of a GeO_4-complex[1] which could in principle have low energy states as well. The as received samples with higher TD concentrations may also contain O-related precipitates. Distinct phonon induced transitions could then be obscured by scattering in a range of phonon wavelengths corresponding to the size distribution of such precipitates[18]. Systematic annealing studies are planned to clarify the situation.

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