Lattice Vibrations of the Cooperites PdO and PtS

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The vibrational spectra of the cooperite type compounds PdO and PtS (space group $P4_2/mmc - D^9_{4h}$, $Z = 2$) are analyzed. Good agreement between experimental and calculated lattice vibration frequencies is obtained using a force field which includes short-range force constants only. This demonstrates a highly covalent bonding character of the cooperites.

Key words: Vibrational spectra, normal coordinate analysis, force constants, cooperite-type compounds

The platinum group chalcogenides PdO and PtS crystallize in the tetragonal cooperite structure [1]. Strong and directed covalent bonds determine this crystal structure. M (M = Pd, Pt) forms four coplanar bonds with X (X = 0, S), which itself is coordinated by four *M* in a distorted tetrahedral environment. The whole three dimensional network of the cooperite structure is built from two sets of chains $^1_\infty[MX_{4/2}]$ directed along [100] and [010] in the tetragonal cell, see Figure 1. The space group of the cooperite structure is $P4_2/mmc$ (D^9_{4h}) and the primitive cell contains two formula units. The positions of the atoms in the unit cell are M: 2(c): 0, 1/2, 0; 1/2, 0, 1/2; X: 2(e): 0, 0, 1/4; 0, 0, 3/4. The 12 vibrational modes ($|\boldsymbol{q}| = 0$) of the unit cell decompose according to the representations:

M(2c):	A_{2u}	$+ B_{2u}$			$+ 2E_u$
X (2e):	$A_{2u} + B_{1g}$			$+ E_g +$	E_u
$\Gamma_{D_{4h}}$(MX):	$2A_{2u} + B_{1g} + B_{2u} + E_g + 3E_u$				
	IR	R	s	R	IR

Of these, one A_{2u} and one E_u are acoustical modes, so that a total of two Raman and three infrared allowed modes is expected in the spectra. All three allowed modes were observed in the infrared spectra of PdO and PtS, whereas the Raman spectrum of PdO shows only one of the two expected modes (Figure 2). In the case of PtS no vibrational Raman spectrum was obtained.

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The infrared spectra of both PdO and PtS show one strong low frequency mode at 160 cm^{-1} and 111 cm^{-1}, respectively, and two less intense modes at higher frequencies (612, 668 cm^{-1} (PdO); 414, 426 cm^{-1} (PtS)). The TO/LO-splittings of the infrared modes are rather small, in accordance with strong covalent but weak ionic bonding contributions [2]. So it must be possible to neglect in a first approximation all long range Coulomb forces and to explain the optical lattice vibrations of the cooperites within a lattice dynamical model which includes short range interactions only.

Symmetry adapted Cartesian coordinates were derived using the projection operator technique [3]. Using these coordinates (Fig. 3), the assignment of the experimental frequencies is straightforward.

The coordinates labeled $q_3(B_{1g})$, $q_4(B_{2u})$, and $q_5(E_g)$ are normal coordinates. The sharp band observed at $\Delta\tilde{\nu} = 652\ cm^{-1}$ in the Raman spectrum of PdO is assigned to the B_{1g} stretching mode. In this

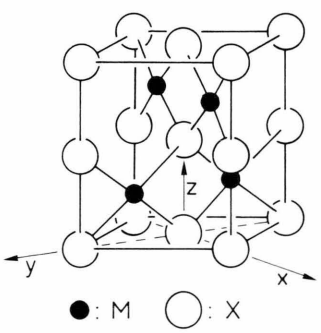

Fig. 1. The crystal structure of cooperite ($P4_2/mmc$, D^9_{4h}).

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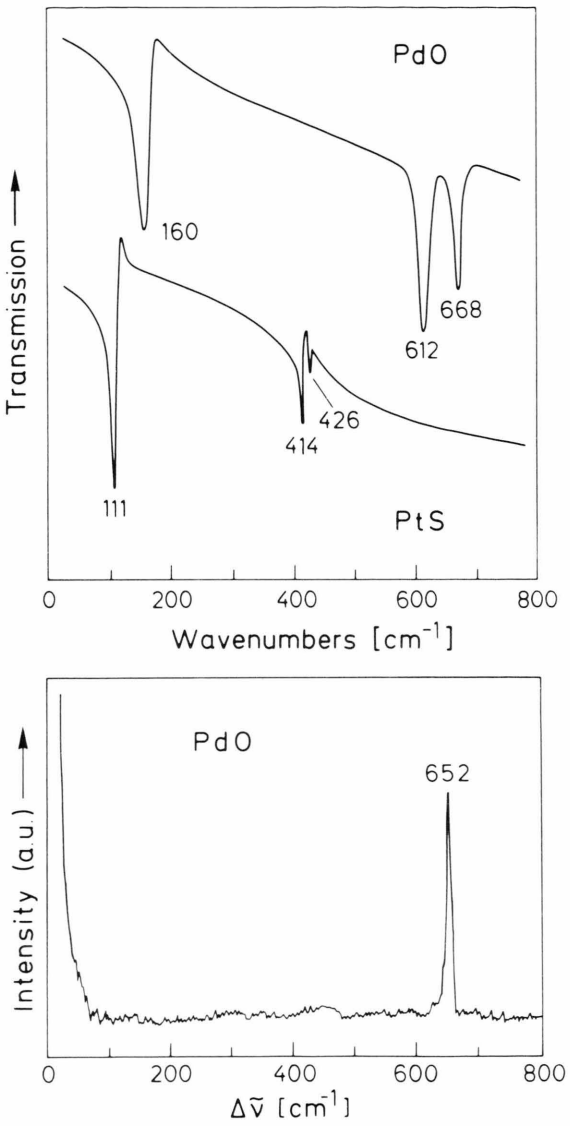

Fig. 2. Infrared absorption spectra of PdO and PtS ($> 500\,cm^{-1}$: KBr pellet, $< 500\,cm^{-1}$: PE pellet, Bruker IFS 113v, room temperature) and Raman spectrum of PdO (pressed pellet).

mode the two oxygen atoms (atoms 3 and 4) move in opposite directions along the z-axis, which will give rise to a high change of the overall polarizability and, therefore, to high Raman scattering intensity. On the other hand, only low intensity is expected for the E_g mode, and its frequency cannot be given from the obtained Raman spectrum.

The linear combinations q_1+q_2 and q_1-q_2 give the acoustical and optical modes of A_{2u} symmetry, respectively, whereas in the case of the E_u modes three symmetry coordinates have to be combined and the normal coordinates cannot be obtained by inspection alone. But simple linear combinations allow for an assignment of the infrared active modes: the linear combination $q_6-q_8(E_u^1)$ represents an out-of-plane bending mode which is expected at lower frequencies, whereas $q_7-q_8(E_u^2)$ is an in-plane mode with both bond stretching and bending character, similar to the A_{2u} optical mode. If it is assumed further that the E_u^2 mode will be more dominant in the infrared spectra than the A_{2u} mode because it is doubly degenerate and has components in both x and y direction, the assignment given in Table 1 results.

This tentative assignment is confirmed by a numerical normal coordinate analysis. The most important force constant (internal coordinate) which must be included in such calculations is the M–X stretching force constant f_1 (e.g. bond between atoms 2 and 3, Figure 3). In calculation 1 (PdO) a value of $f_1 = 2.1\,N\,cm^{-1}$ fits the A_{2u} mode frequency and represents the observed B_{1g} and E_u^2 frequencies surprisingly well (the E_u^1 mode cannot be obtained from f_1 because f_1 has no components perpendicular to the MX_4 plane) and only minor refinements are necessary to improve the calculation. Two possibilities exist to calculate the E_u^1 mode: the introduction of an out of plane bending force constant can be used to reproduce the E_u^1 mode exactly, but such a force constant has no influence on the other vibrational frequencies, and the fit of these modes is not improved. On the other hand, by choosing an appropriate value for the diagonal stretching force constant f_2, i.e. the interaction between M and the next nearest X (e.g. interaction between atoms 2 and 4″, Fig. 3), the E_u^1 mode can be also exactly reproduced but simultaneously an improvement of the total fit is achieved by a slight change of f_1 (calc. 2). In calculation 3 a third force constant (f_3), which represents an interaction between the X-atoms within the $^1_\infty[MX_{4/2}]$-chains (e.g. interaction between atoms 3 and 4) was introduced to give a final fit for the B_{1g} mode. The so obtained force constants $f_1 = 1.99$ and $f_2 = 0.186\,N\,cm^{-1}$ were applied to calculate the vibrational frequencies of PtS (calc. 1). The calculated frequencies (A_{2u}: $476\,cm^{-1}$; E_u^1: $118\,cm^{-1}$; E_u^2: $435\,cm^{-1}$) are higher than those observed. This is in accordance with the Siebert formula [4]

$$f(M-X) = 7.2\,\frac{Z_M\,Z_X}{n_M^3\,n_X^3}$$

Table 1. Experimental and calculated lattice vibration frequencies [cm^{-1}], force constants [N cm^{-1}], potential energy distribution [%], and mass-adjusted L_{XSM}-eigenvectors [7] (E_u^1: y, E_u^2: x-components of the degenerate sets) for the cooperites PdO ($a = 3.043$ Å, $c = 5.337$ Å) and PtS ($a = 3.470$ Å, $c = 6.109$ Å).

	PdO						PtS					L_{XSM}-matrix (E_u) PdO and PtS		
	Frequencies			PED (calc. 3)			Frequencies		PED (calc. 2)					
	$\tilde{\nu}_{exp}$	$\tilde{\nu}_{calc}$ (1)	(2)	(3)	f_1	f_2	f_3	$\tilde{\nu}_{exp}$	$\tilde{\nu}_{calc}$ (1)	(2)	f_1	f_2	q_6	q_7	q_8
B_{1g}	652	622	623	652	86	5	9		441	395	94	6			
E_g		502	554	554	78	22	0		391	354	75	25			
A_{2u}	668	668	668	668	95	5	0	426	476	425	94	6			
B_{2u}		241	242	242	95	5	0		179	160	94	6			
E_g	160	0	160	160	12	88	0	111	118	112	14	86	−0.62	0.75	−0.23
E_u	612	572	611	611	82	18	0	414	435	393	80	20	0.08	0.42	−0.90
f_1(2.024 Å)		2.1	2.0	2.0				(2.312 Å)	2.0	1.6					
f_2(3.654 Å)			0.19	0.19				(4.169 Å)	0.19	0.17					
f_3(2.668 Å)				0.09											

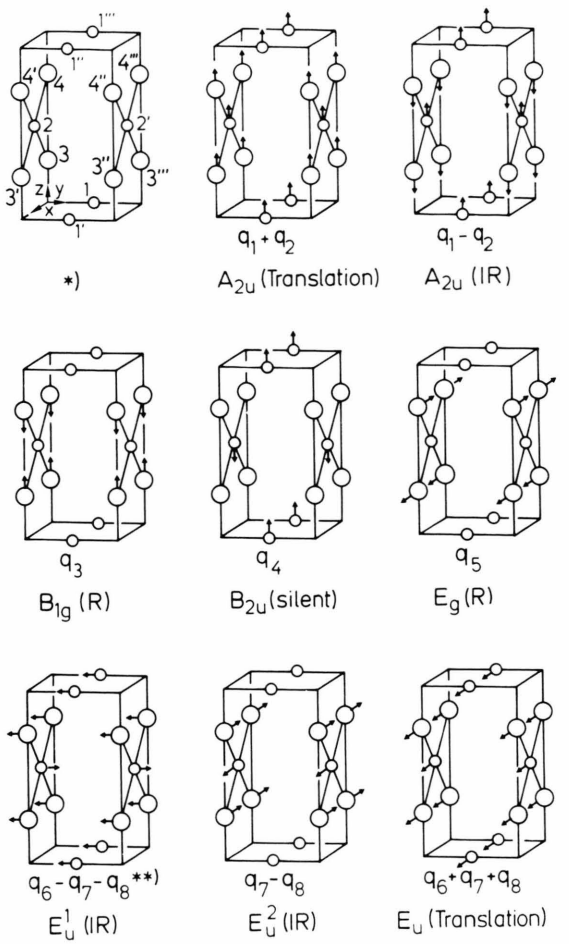

Fig. 3. Atomic positions and displacement of ions for the lattice vibrations of the cooperite structure ($P4_2/mmc$, D_{4h}^9). *) atomic position: 1: (M): 0, 1/2, 0; 2: (M): 1/2, 0, 1/2; 3:(X): 0, 0, 1/4; 4:(X): 0, 0, 3/4.
Symmetry adapted Cartesian coordinates: $q_1 = z_1 + z_2$, $q_2 = z_3 + z_4$ (A_{2u}); $q_3 = z_3 - z_4$ (B_{1g}); $q_4 = z_1 - z_2$ (B_{2u}); $q_5 = x_3 - x_4 (y_3 - y_4)$ (E_g); $q_6 = x_1 (y_1)$; $q_7 = x_2 (y_2)$, $q_8 = x_3 + x_4 (y_3 + y_4)$ (E_u).
**) The y-component of the degenerate E_u mode is shown.

(Z = atomic number, n = period number), which predicts $f(\mathrm{Pt-S}) = 1.54\ \mathrm{N\,cm^{-1}} < f(\mathrm{Pd-O}) = 2.65\ \mathrm{N\,cm^{-1}}$. Decreasing f_1 and f_2 leads to a satisfactory agreement between observed and calculated infrared active modes of PtS.

The results are summarized in Table 1. The displacements of the atoms for the E_u^1 and E_u^2 modes (Fig. 3) clearly show the out of plane bending character of the lowest frequency modes of the cooperites, as was expected above from the qualitative discussion.

$f_1 = 1.99\,\mathrm{N\,cm^{-1}}$ (PdO) can be compared with $f(\mathrm{Pd-O}) = 1.85\,\mathrm{N\,cm^{-1}}$ found in the complex palladium salt $\mathrm{Pd(acac)_2}$, for which $d(\mathrm{Pd-O}) = 1.95$ Å [5].

Experimental

PtS was prepared by annealing stoichiometric mixtures of the elements in evacuated quartz tubes at 700 °C/10 d, PdO by heating palladium powder in an oxygen atmosphere at 650 °C/6 d. Pressed pellets of the compounds were used to measure the Raman spectra in a conventional back scattering configuration using a Jarrell Ash double monochromator, RCS photomultiplier and Spectra Physics Ar and Kr laser sources. The infrared spectra were obtained using a Bruker IFS 113v Fourier transform interferometer. The normal coordinate analysis was performed using Wilson's GF-matrix method [3] in the version similar to that extended by Shimanouchi [6] for the calculation of the optically active ($|\boldsymbol{q}| = 0$) lattice vibration frequencies.

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