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Absorption Spectra of PbF, PbCl and PbBr

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A vibrational analysis has been made of absorption band systems due to PbF, PbCl, and PbBr. A single system of double-headed bands lying between λλ4100 and 5300A has been observed for PbF. The separation of the heads is nearly constant. In PbCl a band system with the origin at 4571.8A has been found for each of the isotopes Cl^{35} and Cl^{37}. Similarly a system of bands between λλ4400 and 5400A has been observed for each of the isotopes Br^{79} and Br^{81}. The vibrational analyses are confirmed by the respective isotope shifts. All the bands degrade to the red.

BARRATT[1] has reported, without analysis, absorption spectra which he attributed to lead chloride. Howell and Rochester[2] have produced emission band spectra in PbF and PbBr by the use of a high frequency electrical discharge, but apparently they did not make a vibrational analysis. No other observations on the band spectra of lead halides seem to have been recorded.

To obtain the band spectra of the lead halides in absorption, the lead halide under investigation was placed in an open iron or graphite tube about 30 cm in length and heated in an electric resistance furnace to such a temperature that the band system was well developed when light from a 500-watt incandescent lamp was passed through the column of vapor. Since PbF, PbCl, and PbBr do not exist as stable chemical compounds, it was necessary to introduce PbF_2, $PbCl_2$, or $PbBr_2$ into the furnace and heat it to a temperature at which it dissociates into the diatomic halide. The PbCl and PbBr systems were well developed at about 900°C, while a temperature of 1500°C was found more suitable for PbF. In the case of lead chloride and lead bromide the band systems were also developed by passing chlorine or bromine, respectively, over molten lead in the electric furnace.

Preliminary observations were made on an E-1 quartz spectrograph, but all measurements were made from spectrograms taken on a 10-ft. concave grating which has a dispersion of 2.72A/mm in the second order. Both first- and second-order plates were measured in each case.

PbF BANDS

In the case of PbF, a double-headed band system, degrading toward the red, was observed. The double heads are separated by about 7 cm^{-1}. Because of overlapping fine structure only one head has been measured in most cases, but where two heads of a given band have been measured the observed wave numbers of both have been tabulated. The vibrational quantum numbers, the estimated intensities, the observed wave numbers, and the difference between the observed and calculated wave numbers for the higher frequency heads are given in Table I. This table also shows the observed wave numbers

TABLE I. *Analysis of PbF band heads.*

v'	v''	I	$\nu_{obs.}$	$\nu_{obs.}-\nu_{calc.}$	v'	v''	I	$\nu_{obs.}$	$\nu_{obs.}-\nu_{calc.}$
8	14	00	18945.4	−4.7	4	5	2	21600.8	0.0
7	13	0	19019.9	−3.6	8	8	0	676.3	0.9
5	11	0	171.7	−1.4	3	4	1	702.8	1.7
3	9	00	328.4	1.5	1	2	5	905.5	0.6
8	13	0	388.9	−3.9	0	1	10	22008.4	−0.1
7	12	0	468.0	−2.6	4	4	2	085.5	0.7
6	11	1	548.0	−1.6	3	3	5	189.4	−0.3
5	10	1	628.1	−1.5	2	2	5	295.1	−0.5
3	8	1	792.9	0.3	1	1	1	405.0	2.3
2	7	0	877.5	1.9	5	4	2	465.7	0.8
7	11	0	921.0	−1.6	0	0		502.9*	
1	6	0	961.1	1.3	0	0	10	510.4	−0.4
6	10	1	20005.2	−0.9	4	3		568.8*	
5	9	1	089.8	−0.9	4	3	1	574.6	1.3
4	8	2	176.5	0.2	7	5	0	728.5	−1.9
3	7	2	263.0	0.2	2	1	5	793.6	0.2
8	11	0	291.3	−0.8	1	0		897.7*	
2	6	2	351.0	0.5	1	0	10	904.8	−0.2
1	5	1	440.0	0.8	4	2	3	23068.6	2.1
0	4	1	529.8	0.8	3	1		174.0*	
5	8	0	556.2	−0.2	3	1	6	180.8	0.2
4	7	1	646.5	0.0	2	0		288.3*	
9	11	0	658.1	0.0	2	0	8	295.6	−0.1
3	6	3	737.7	0.0	5	2	2	447.7	1.1
2	5	5	830.2	0.3	4	1		557.3*	
1	4		916.2*		4	1	4	564.6	0.3
1	4	6	923.6	0.4	3	0	5	682.9	0.0
0	3		21010.0*		6	2	1	825.1	2.0
0	3	5	017.8	0.2	5	1		938.4*	
3	5	1	216.0	−1.1	5	1	3	945.4	1.0
2	4	4	313.9	0.0	4	0	1	24068.0	1.4
1	3		404.0*		8	3	0	074.7	2.2
1	3	7	411.9	0.1	7	2	0	199.9	3.8
0	2		502.3*		6	1		315.4*	
0	2	8	510.7	0.0	6	1	0	322.8	1.9

* Indicates lower frequency head of band.

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[1] Barratt, Trans. Faraday Soc. **25**, 758 (1929).

[2] Howell and Rochester, Univ. Durham Phil. Soc. Proc. **9**, 126 (1934).

and the vibrational quantum numbers of the lower frequency band heads which could be measured. These lower frequency heads have been marked with an asterisk. The higher frequency heads are represented by the formula:

$$\nu = 22{,}565.2 + [397.8u' - 1.77u'^2] - [506.9u'' - 2.29u''^2],$$

where $u' = v' + \frac{1}{2}$ and $u'' = v'' + \frac{1}{2}$. They appear to be of greater intensity than the lower frequency ones. The intensity distribution of these bands is shown in Table II.

PbCl BANDS

One system for each of the isotopes of chlorine, Cl^{35} and Cl^{37}, has been observed for PbCl. The bands degrade to the red and in some cases appear to be double-headed with a very small separation between the two heads. The vibrational analysis of these band heads is given by the formulas:

$$PbCl^{35}:\ \nu = 21{,}866.9 + [228.6u' - 0.76u'^2 - 0.006u'^3] - [304.2u'' - 0.89u''^2];$$

$$PbCl^{37}:\ \nu = 21{,}866.9 + [223.3u' - 0.72u'^2 - 0.006u'^3] - [297.1u'' - 0.85u''^2],$$

where $u' = v' + \frac{1}{2}$ and $u'' = v'' + \frac{1}{2}$. The constants of the second equation have been calculated from those of the first equation by the use of the formula $G^i(v) = \rho\omega_e(v+\frac{1}{2}) - \rho^2 x_e\omega_e(v+\frac{1}{2})^2 + \cdots$, where $G^i(v)$ is the vibrational term for the isotope and ρ is the square root of the ratio of the reduced masses of the two molecules. The analysis of the PbCl bands is recorded in Table III and the distribution of estimated intensities for the $PbCl^{35}$ bands is shown by Table IV. The ratio of the intensities of the bands of $PbCl^{35}$ and $PbCl^{37}$ is approximately the ratio (76 : 24) of the abundance of the chlorine isotopes.

PbBr BANDS

As in the case of PbCl, one system of bands has been observed for each of the isotopes of bromine. These bands also degrade to the red and the band-intensity curve is a parabola

TABLE II. *Intensities of bands in PbF.*

v' \ v''	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
0	10	10	8	5	1										
1	10	1	5	7	6	1	0								
2	8	5	5		4	5	2	0							
3	5	6		5	1	1	3	2	1	00					
4	1	4	3	1	2	2		1	2						
5	0	3	2		2				0	1	1	0			
6		0	1								1	1			
7			0			0						0	0	0	
8				0					0			0		0	0
9												0			

TABLE IV. *Intensities of $PbCl^{35}$ bands.*

v' \ v''	0	1	2	3	4	5	6	7	8	9	10
0	4	2	4	8	7	4	2	1	0		
1	2	8	10	3	00		1	2	2	0	
2	6	10	4		1	2	0		0	1	0
3	5	7		1	2			0	0		
4	6	2		00						0	
5	7		1								
6	4		2								
7	3	0	0								
8	2	1									
9	1	1									
10	1	2									
11	1	3	0								
12		1	1								
13		0	0								

TABLE III. *Analysis of PbCl bands.*

v'	v''	I	$\nu_{obs.}(PbCl^{35})$	$\nu_{obs.}-\nu_{calc.}$	$\nu(PbCl^{35})-\nu(PbCl^{37})$ Obs.	$\nu(PbCl^{35})-\nu(PbCl^{37})$ Calc.
2	10	0	19338.3	0.7		
1	9	0	399.1	0.6		
0	8	0	459.9	0.3		
2	9	1	624.8	0.8		
1	8	2	687.2	0.5	−49.0	−49.6
0	7	1	749.0	−0.6	−47.3	−48.3
2	8	0	911.9	−0.3		
1	7	2	977.2	0.5	−43.7	−43.1
0	6	2	20041.5	0.2	−42.4	−41.8
4	9	0	069.6	−0.5		
3	8	0	135.6	−0.4		
1	6	1	268.8	0.4	−38.1	−36.6
0	5	4	335.1	0.3	−34.1	−35.2
3	7	0	426.1	0.1		
2	6	0	494.4	0.5		
0	4	7	630.2	0.1	−29.0	−28.5
2	5	2	788.0	0.6	−25.4	−24.8
1	4	00	858.1	0.9		
0	3	8	927.1	−0.1	−22.3	−21.7
2	4	1	21083.8	1.1	−18.1	−18.1
1	3	3	154.8	0.5	−16.1	−16.5
0	2	4	226.2	0.1	−14.4	−14.8
3	4	2	306.9	0.4	−11.2	−13.1
1	2	10	453.1	−0.1	−10.4	−9.6
0	1	2	528.0	1.3	−5.1	−7.9
3	3	1	603.8	0.2		
2	2	4	679.0	−0.3	−5.4	−4.4
1	1	8	753.2	−0.6	−3.0	−2.7
4	3	00	825.7	−0.2		
0	0	4	829.8	0.7		
2	1	10	978.5	−0.8	3.8	2.5
1	0	2	22057.0	0.8	5.5	4.3
3	1	7	202.6	−0.5	7.8	7.5
2	0	6	281.2	−0.5	10.7	9.5
5	2	1	345.1	−0.2	12.5	10.5
4	1	2	425.0	−0.4	13.3	12.6
3	0	5	505.8	0.3	15.0	14.5
6	2	2	563.2	−0.9	16.0	15.3
4	0	6	727.4	−0.4	19.9	19.6
7	2	0	781.8	0.6		
5	0	7	949.1	0.8	23.9	24.4
7	1	0	23083.4	1.6		
6	0	4	168.1	1.0	30.1	29.2
8	1	1	297.4	0.3		
7	0	3	384.8	0.6	33.5	33.9
9	1	1	511.0	0.4		
8	0	2	600.2	0.7	38.3	38.6
11	2	0	632.6	1.3		
10	1	2	722.9	0.7	38.9	40.8
9	0	1	815.4	2.4		
12	2	1	836.8	−2.2		
11	1	3	931.0	−0.9	43.9	45.1
10	0	1	24025.5	0.9		
13	2	0	037.6	−7.2		
12	1	1	137.3	−2.3	48.8	49.4
11	0	1	233.8	−0.5		
13	1	0	337.9	−7.5	51.7	53.7

TABLE V. *Analysis of PbBr bands.*

v'	v''	I	$\nu_{\text{obs.}}(\text{PbBr}^{79})$	$\nu_{\text{obs.}}-\nu_{\text{calc.}}$	$\nu(\text{PbBr}^{79})-\nu(\text{PbBr}^{81})$		v'	v''	I	$\nu_{\text{obs.}}(\text{PbBr}^{79})$	$\nu_{\text{obs.}}-\nu_{\text{calc.}}$	$\nu(\text{PbBr}^{79})-\nu(\text{PbBr}^{81})$		v'	v''	I	$\nu_{\text{obs.}}(\text{PbBr}^{79})$	$\nu_{\text{obs.}}-\nu_{\text{calc.}}$	$\nu(\text{PbBr}^{79})-\nu(\text{PbBr}^{81})$	
					Obs.	Calc.						Obs.	Calc.						Obs.	Calc.
1	11	0	18790.9	−1.0	−17.8	−18.5	2	4	1	339.0	0.0	−5.2	−5.0	6	3	1	132.2	1.4		
1	10	1	988.6	0.2	−14.9	−16.8	1	3	8	391.8	−0.1	−4.4	−4.5	5	2	0	190.3	−0.3		
0	9	2	19034.9	0.6	−15.6	−16.5	4	5	0	432.4	−1.4			4	1	4	249.4	−0.4	3.2	3.2
0	8	4	233.5	0.7	−13.2	−14.8	2	3	7	543.4	0.9	−3.2	−3.2	7	3	1	275.1	1.5	3.1	2.9
1	8	1	382.8	−1.6	−12.7	−13.4	1	2	3	597.7	1.3			3	0	0	309.1	0.8	4.3	3.8
0	7	6	432.7	0.4	−12.3	−13.2	4	4	0	638.6	2.3			5	1	5	396.4	0.3	4.7	4.3
2	8	2	535.6	0.6	−11.1	−12.1	7	6	00	667.8	1.7	−2.7	−2.5	4	0	2	455.5	−0.8	6.2	5.1
0	6	7	632.9	0.1	−10.9	−11.3	3	3	2	692.8	1.0			7	2	0	475.4	−2.7		
2	7	2	733.7	−0.6	−10.7	−10.4	2	2	8	747.6	0.6	−1.4	−1.4	6	1	3	540.9	0.1	5.2	5.5
1	6	1	785.2	1.1	−8.9	−9.9	5	4	1	784.1	1.5			5	0	5	602.1	−0.5	6.0	6.2
0	5	8	834.3	0.0	−8.9	−9.5	1	1	1	801.5	−0.4			8	2	0	620.2	1.4	5.2	5.8
2	6	0	933.4	−0.6	−8.7	−8.6	3	2	5	896.5	0.2			7	1	1	685.9	2.3	7.7	6.6
1	5	7	986.3	0.4	−7.8	−8.1	6	4	0	929.0	1.7			6	0	7	746.8	−0.5	6.6	7.4
0	4	5	20036.8	0.0	−7.3	−7.7	2	1	3	951.5	−1.0			8	1	00	829.6	5.3		
3	6	3	084.8	0.8	−6.8	−7.2	5	3	0	987.6	1.5			7	0	9	890.4	0.3	8.1	8.5
1	4	8	188.2	−0.2	−6.3	−6.3	1	0	0	21011.6	3.2			8	0	8	22032.2	1.4	10.3	9.6
0	3	2	240.4	0.1	−5.7	−5.9	4	2	3	044.5	0.2			9	0	7	169.1	−0.2	10.8	10.5
3	5	0	286.9	1.1	−4.4	−5.4	3	1	4	101.2	−0.6	2.5	1.9	10	0	6	303.4	−2.0	12.1	11.5

somewhat wider than the Franck-Condon parabola for PbCl^{35}. The intensities of corresponding band heads for the two isotopes are nearly equal as might be expected from the abundance ratio (1 : 1) of the two isotopes of bromine. In some cases these bands also appear to be double-headed. They are much less sharp than the bands of PbF or PbCl. Table V gives the vibrational analysis, the observed wave numbers for PbBr^{79}, the difference between the observed and calculated wave numbers and a comparison between the observed and calculated isotope shift. The following equations give the wave numbers of the band heads, the equation for PbBr^{81} being calculated from that for PbBr^{79}.

$$\text{PbBr}^{79}:\ \nu=20{,}884.3+[152.5u'-0.40u'^2-0.028u'^3]-[207.5u''-0.50u''^2];$$

$$\text{PbBr}^{81}:\ \nu=20{,}884.3+[151.1u'-0.39u'^2-0.027u'^3]-[205.6u''-0.49u''^2],$$

where $u'=v'+\frac{1}{2}$ and $u''=v''+\frac{1}{2}$.

DISCUSSION

A striking similarity is noted between the lead halide bands and the longer wave-length systems of the bismuth halides.[3] In all cases the corresponding constants are nearly the same, as might be expected since the atomic weights of lead and bismuth are 207.22 and 209.00, while the charges are 82 and 83, respectively. The system origin of the PbF bands lies slightly to the red of the origin of the BiF bands, while the reverse is true in the case of the PbCl and PbBr and the corresponding bismuth halide bands.

From the similarity of the PbF, PbCl and PbBr molecules, the PbCl and PbBr systems would be expected to be double-headed if the corresponding system due to PbF were double-headed. However, since the Franck-Condon parabola is more open for PbCl and PbBr than for PbF, the separation between a band head and the origin of the band should be less for PbCl and PbBr than for PbF. Consequently the separation between the two heads of a double-headed band would be less for a PbCl or a PbBr band than for a PbF band. In the case of the PbF bands this separation was large enough to measure but it could not be observed with certainty in the case of either PbCl or PbBr. That the two heads, observed in the case of PbF, are not due to lead isotopes is evident since the maximum isotope shift in the case of Pb^{208}F and Pb^{206}F would be only about 1 cm^{-1}. Also if the two heads were the result of isotopy, the separation should increase almost linearly with the distance from the system origin while the observed separation between heads is almost constant.

Lead and tin are in the same subgroup in the periodic table. Since the number of electrons is odd for the halides of both tin and lead, the spin number must be half-integral. Hence a doublet system of levels may be expected and from the electron configuration the halides of both tin and lead might be expected to have a

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[3] F. Morgan, "Band Spectra of BiBr, BiCl, BiF and BiI in Absorption," this issue.

$^2\Pi$ ground state. Jevons[4] and Ferguson[5] have analyzed the emission spectra of SnCl and found two systems having a common lower $^2\Pi$ state with a doublet separation of about 2360 cm^{-1}. They, however, observed the bands in emission and it is not certain that the $^2\Pi$ state is the ground state. The lowest state of the PbCl bands reported here must be the ground state since the bands were observed in absorption. If the lower state of the bands of Jevons and Ferguson corresponds to the ground state of PbCl, then the ground state of PbCl would be expected to be a $^2\Pi$ state with a doublet separation of approximately 7000 cm^{-1}. Such a separation would place the origin of the other part of a doublet system in the neighborhood of either 7000A or 3500A. No sub-system was observed in either of these regions. Such a system should have been easily observed had it been in the vicinity of 3500A since the intensity of the high frequency part of the doublet system should be greater than the intensity of the low frequency part. However, if the sub-system were in the neighborhood of 7000A it would probably not have been observed in absorption, since even at 1600°C the intensity of the high frequency part would be expected to be about 750 times that of the other.

The author wishes to express his appreciation to Professors Alpheus W. Smith, J. B. Green, and R. V. Zumstein for valuable discussions and suggestions given during the course of this investigation.

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[4] W. Jevons, Proc. Roy. Soc. **A110**, 365 (1926).

[5] W. F. C. Ferguson, Phys. Rev. **32**, 607 (1926).

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The Variation of the Adiabatic Elastic Moduli of Rocksalt with Temperature Between 80°K and 270°K

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The piezoelectric method devised by Balamuth for measuring Young's modulus of a cubic crystal for any chosen direction has been extended to permit the measurement of all the elastic moduli of any solid crystal at temperatures below 0°C. Data are given which show the variation of the adiabatic and isothermal elastic moduli and elastic constants of rocksalt with temperature between 80°K and 270°K.

INTRODUCTION

IN a recent issue of this journal Dr. Lewis Balamuth has described a method for measuring Young's modulus corresponding to any chosen direction in a solid crystalline substance.[1] This method utilizes the properties of a separately excited composite piezoelectric oscillator constructed by cementing an X-cut cylinder of quartz to one end of a cylinder of specimen material. The fundamental frequency of free longitudinal vibration of this system is measured by observing the variation of its electrical reactance with the frequency of the applied voltage, and Young's modulus of the specimen material for the direction of the cylinder axis is calculated from this and other readily measurable quantities. Now measurements of Young's modulus for various directions in a crystal yield some but not all its elastic constants, while the remainder can be calculated if, in addition, one or more rigidity moduli are known. The object of the present paper is to describe a method for measuring the rigidity modulus corresponding to any chosen direction in a crystal.

The success of Balamuth's method depends upon the fact that the electrically excited quartz crystal produces longitudinal vibration of sufficient purity along the whole oscillator. Now Giebe and Scheibe[2] have shown that a suitably cut cylinder of quartz can be excited to torsional

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[1] L. Balamuth, Phys. Rev. **45**, 715 (1934); **46**, 933 (1934).

[2] Giebe and Scheibe, Zeits. f. Physik **46**, 607 (1928).