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Lattice-Dynamical Calculations for Zinc and Beryllium

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Phonon dispersion curves for zinc and beryllium, measured by neutron-inelastic-scattering techniques, have been used to determine the atomic force constants for the modified axially symmetric model developed by DeWames, Wolfram, and Lehman. However, calculations have revealed that statistically equivalent fits to the experimental data may be obtained from more than one set of parameters.

The modified axially symmetric model is based upon the harmonic approximation, has a total of 18 free parameters, and includes interactions out to the sixth nearest neighbors. This model was developed by DeWames, Wolfram, and Lehman (DWL),[1] and used by them to fit the experimental phonon curves for zinc and beryllium. They indicated that a total of 18 parameters was needed to obtain a reasonable fit for zinc, while 13 parameters were needed for beryllium.

Using their parameters as starting values, and a general least-squares fitting routine, we have found that adjustment of their parameter values would produce significantly better fits to the neutron data than those obtained by DWL. More important, however, is our discovery that the fits are not unique. By assigning arbitrary starting values to the various parameters we have found, for both zinc and beryllium, different sets of parameters that will produce statistically equivalent fits.

ZINC

Table I is a compilation of results derived from DWL[1] together with some of our results for zinc. All results are based upon the same experimental neutron data.[2] Column A lists DWL values as used in our program. The variance of the fit calculated from this set is $F = 3.96$ with 30 of the points calculated for the dispersion curves lying outside the experimental error assigned to the corresponding experimental points. (For both zinc and beryllium, parameters were determined using 52 points taken from the measured dispersion curves. Included were the two optical intercepts plus five points, evenly spaced at intervals of 0.2 $q/q_{\max}$, chosen from each of the 10 branches). Column B lists the parameters obtained after adjustment of the values in column A with our program. In addition, we include the calculated error (or "measure of confidence"). DWL did not list errors for their values, so we have not included them in column A. For column B, we have $F = 0.87$ and only 10 of the calculated points lie outside of experimental error.

Note that, for column B, certain of the parameters have large errors relative to their calculated values, an indication that the fit is not sensitive to these particular parameters. (This unexpected piece of information was, in fact, the stimulus for our investigation.) One might as well set these parameters equal to zero, and calculate a new fit. Column C lists the results of such a procedure, where now $F = 2.11$ and 19 points lie outside experimental error.

At this juncture we decided to assign arbitrary starting values (1.0) to arbitrary groups of parameters. Column D shows one set of results, in which only 7 parameters were allowed to vary, the rest being set equal to zero. Here $F = 1.59$ and 20 points are outside experimental error. Note that although some parameters have changed sign as well as magnitude, still the fit to the neutron data is equivalent, if not superior, to that obtained by DWL. The set of parameters in column D is stable with respect to a hundredfold change in starting values. We doubt that it is unique.

TABLE I. Zinc: atomic force constants (units of 10^4 dyn/cm).

	Calculation			
Parameter[a]	A	B	C	D
$K(1, 11)$	2.67	2.63 ± 0.04	2.47 ± 0.03	2.49 ± 0.03
$C_{Bx}(1, 11)$	−0.10	−0.01 ± 0.04		
$C_{Bz}(1, 11)$	−0.35	0.31 ± 0.03	−0.27 ± 0.01	−0.30 ± 0.01
$K(2, 12)$	0.83	0.85 ± 0.24	0.80 ± 0.02	0.70 ± 0.02
$C_{Bx}(2, 12)$	−0.10	−0.11 ± 0.04	−0.11 ± 0.03	
$C_{Bz}(2, 12)$	−0.09	−0.07 ± 0.17		
$K(3, 12)$	0.42	0.59 ± 0.09	0.60 ± 0.11	
$C_{Bx}(3, 12)$	−0.07	−0.12 ± 0.03	−0.11 ± 0.04	0.06 ± 0.01
$C_{Bz}(3, 12)$	−0.02	−0.10 ± 0.04	−0.07 ± 0.04	0.25 ± 0.01
$K(4, 11)$	−0.20	−0.07 ± 0.04		
$C_{Bx}(4, 11)$	0.08	−0.03 ± 0.03		
$C_{Bz}(4, 11)$	0.06	0.01 ± 0.02		
$K(5, 12)$	0.07	0.01 ± 0.05		
$C_{Bx}(5, 12)$	0.03	0.05 ± 0.02	0.04 ± 0.01	
$C_{Bz}(5, 12)$	0.04	0.04 ± 0.02		
$K(6, 11)$				
$C_{Bz}(6, 11)$	−0.15	−0.25 ± 0.02	−0.23 ± 0.04	−0.25 ± 0.03
$C_{Bx}(6, 11)$	0.06	0.12 ± 0.01	0.14 ± 0.02	0.14 ± 0.02
F (variance)	3.96	0.87	2.11	1.59

[a] Notation is that of DWL (Ref. 1), where (p, mn) denotes the interaction of the nth atom of the pth shell with the mth atom in the cell at the origin.

TABLE II. Zinc: elastic constants (units of 10^{12} dyn/cm^2).

Elastic constant	Experimental[a]	Calculation				Equation[c]
		A[b]	B	C	D	E
C_{11}	1.637	1.543(1.539)	1.48 ± 0.10	1.56 ± 0.10	1.39 ± 0.11	i
		1.543	1.48 ± 0.10	1.56 ± 0.10	1.39 ± 0.11	$\frac{1}{2}$(ii + iv)
C_{12}	0.364	0.366(0.362)	0.58 ± 0.09	0.58 ± 0.11	0.40 ± 0.09	$\frac{1}{2}$(iv − ii)
		0.366	0.58 ± 0.09	0.58 ± 0.11	0.40 ± 0.08	i − ii
		0.366	0.58 ± 0.12	0.58 ± 0.13	0.40 ± 0.10	iv − i
C_{13}	0.530	0.442	0.54 ± 0.10	0.61 ± 0.09	0.09 ± 0.13	v − vi
		0.390(0.385)	0.32 ± 0.11	0.30 ± 0.10	0.16 ± 0.19	v − iii
C_{33}	0.635	0.682(0.678)	0.51 ± 0.11	0.53 ± 0.10	0.51 ± 0.11	vii
C_{44}	0.388	0.265	0.18 ± 0.14	0.10 ± 0.12	0.15 ± 0.10	vi
		0.317(0.315)	0.39 ± 0.13	0.41 ± 0.14	0.42 ± 0.13	iii

[a] From ultrasonic measurements (Ref. 3).

[b] Values in parentheses are taken from DWL and are not necessarily associated with the equation numbers in column E.

[c] Equations (8) of Ref. 1 have been numbered i through vii in sequence.

Elastic constants and calculated errors are presented in Table II, where columns A–D correspond to the parameter sets of columns A–D in Table I. DWL list 7 independent equations for the 5 elastic constants: Seeing no reason to prefer any particular equation, we list the results from all 7 in Table II; the actual equations used are indicated in column E. Note in column A that certain of our values agree closely with DWL, indicating to us that our program reproduces their results correctly.

The agreement between the elastic constants calculated from the various parameter sets A–D is reasonable, with one exception: C_{13} for column D is essentially undetermined. We can correct this problem by constraining our program to simultaneously fit the experimental (ultrasonic) elastic constants at the expense of the fit to the neutron data. However, since there exists some question regarding this constraint,[4-6] we chose to use only the neutron data for the determination of parameters, and to forego attempts to obtain a "best" fit by adjusting to both neutron and ultrasonic data. That such attempts would be of limited value appears to be indicated by the existence of different parameter sets which do not converge to a common set.

TABLE III. Beryllium: atomic force constants (units of 10^4 dyn/cm).

Parameter[a]	Calculation		
	A	B	C
$K(1, 12)$	2.22	2.21 ± 0.24	2.71 ± 0.11
$C_{Bx}(1, 12)$	0.14	0.24 ± 0.10	−0.14 ± 0.09
$K(2, 11)$	1.36	0.97 ± 0.11	0.71 ± 0.14
$C_{Bx}(2, 11)$	0.08	0.21 ± 0.08	0.52 ± 0.13
$K(3, 12)$	1.20	−0.77 ± 0.37	−0.63 ± 0.18
$C_{Bx}(3, 12)$	−0.27	0.14 ± 0.13	0.21 ± 0.08
$K(4, 11)$	0.20	0.73 ± 0.12	0.72 ± 0.08
$C_{Bx}(4, 11)$	0.32	0.41 ± 0.04	0.40 ± 0.05
$K(5, 12)$	−0.07	0.19 ± 0.07	0.61 ± 0.07
$C_{Bx}(5, 12)$	0.15	0.08 ± 0.04	0.01 ± 0.02
$K(6, 11)$	0.31	0.59 ± 0.07	0.21 ± 0.08
$C_{Bx}(6, 11)$	0.03	0.09 ± 0.07	0.13 ± 0.09
σ_B	1.31	0.97 ± 0.19	0.46 ± 0.13
F (variance)	3.49	0.98	1.57

[a] Notation is that of DWL (Ref. 1), where (p, mn) denotes the interaction of the nth atom of the pth shell with the mth atom in the cell at the origin.

BERYLLIUM

In the case of beryllium, the calculational procedure is somewhat modified. DWL made the

TABLE IV. Beryllium: elastic constants (units of 10^{12} dyn/cm^2).

Elastic constant	Experimental[a]	Calculation			Equation[c]
		A[b]	B	C	D
C_{11}	2.994	2.946(2.955)	2.99 ± 0.14	3.05 ± 0.08	i
		2.946	2.99 ± 0.13	3.05 ± 0.09	$\frac{1}{2}$(ii + iv)
C_{12}	0.276	0.327(0.316)	0.10 ± 0.35	0.19 ± 0.10	$\frac{1}{2}$(iv − ii)
		0.327	0.20 ± 0.25	0.19 ± 0.11	i − ii
		0.327	0.10 ± 0.45	0.19 ± 0.09	iv − i
C_{13}	0.110	0.234	0.21 ± 0.23	0.46 ± 0.11	v − vi
		0.173(0.174)	0.18 ± 0.24	0.15 ± 0.09	v − iii
C_{33}	3.422	3.355(3.377)	3.91 ± 0.12	3.64 ± 0.11	vii
C_{44}	1.662	1.530	1.24 ± 0.10	1.31 ± 0.11	vi
		1.591(1.600)	1.61 ± 0.08	1.61 ± 0.07	iii

[a] From ultrasonic measurements (Ref. 8).

[b] Values in parentheses are taken from DWL and are not necessarily associated with equation numbers in column D.

[c] Equations (8) of Ref. 1 have been numbered i through vii in sequence.

TABLE V. Beryllium: atomic force parameters (in units of 10^4 dyn/cm).

Parameter[a]	Calculation A	B
$K(1,\ 12)$	-2.02 ± 0.13	0.45 ± 0.34
$C_{Bx}(1,\ 12)$	0.58 ± 0.12	
$C_{Bz}(1,\ 12)$	2.42 ± 0.40	0.81 ± 0.24
$K(2,\ 11)$	0.78 ± 0.20	0.88 ± 0.22
$C_{Bx}(2,\ 11)$	0.82 ± 0.12	0.77 ± 0.13
$C_{Bz}(2,\ 11)$	-0.02 ± 0.08	
$K(3,\ 12)$	0.93 ± 0.28	1.44 ± 0.29
$C_{Bx}(3,\ 12)$	0.30 ± 0.09	0.26 ± 0.10
$C_{Bz}(3,\ 12)$	0.54 ± 0.11	0.36 ± 0.12
$K(4,\ 11)$ $+C_{Bz}(4,\ 11)$	0.97 ± 0.15	0.98 ± 0.15
$C_{Bx}(4,\ 11)$	0.37 ± 0.66	0.39 ± 0.07
F (variance)	2.74	3.38

[a] Notation is that of DWL (Ref. 1), where (p, mn) denotes the interaction of the nth atom of the pth shell with the mth atom in the cell at the origin.

assumption that the bending constants for each of the 6 shells are in proportion, and further, that the constants of proportionality are all equal. This has the effect of reducing the number of free parameters in the model from 18 to 13.

Table III is a presentation of our results using this 13-parameter method. Again, column A lists DWL values as used in our program. Here, $F = 3.49$ and 24 points are outside experimental error. [Our results, along with those of DWL, are based upon the same experimental data.[7]] Column B is obtained from column A in the manner described previously and yields $F = 0.98$ with 15 points lying outside of experimental error. Column C is the result of assigning arbitrary starting values (1.0 to all parameters in this case) to the 13 parameters. Here, $F = 1.57$ and only 12 points lie outside of experimental error. Note that some parameters have changed sign, in addition to magnitude. Elastic constants, calculated from the different sets of parameters, are displayed in Table IV. Note that the adjustment of DWL values has yielded values of C_{12} and C_{13} that are essentially undetermined, even though all 13 parameters have been used.

Seeing no good physical reason for the DWL assumption concerning the bending force constants, we tried some calculations without this restriction. Table V presents some of our results. Column A lists results for a calculation in which we arbitrarily chose 11 parameters (those associated with the first 4 shells) and assigned to each of them an initial value of 1.0. All other parameters are set equal to zero. Here, $F = 2.74$ and 23 points are outside of experimental error. Although we have used only 11 parameters and 2 fewer shells than did DWL, still the neutron data is fit as well as with their work. Column B lists results for a similar calculation, but involving only 9 parameters, again with initial values of 1.0. F is 3.38 and 25 points lie outside experimental error. Note the changes in sign, as well as magnitude, between the values listed in the two columns.

We do not claim that this set (column B) is unique, nor even that it is the "best" set; we remark only that this set is stable with respect to a hundredfold change in starting values. Elastic constants C_{12} and C_{13} are not determined (Table VI), which is similar to result obtained from adjusted DWL values (Table III, column B). However, as for zinc, this situation could be rectified by requiring the program to fit the elastic constants in addition to the neutron data.

CONCLUSION

In these types of calculations, it is clear that one should always investigate the uniqueness of the parameter set obtained. At the very least, the stability of the set with respect to initial values should be tested, a simple task on a high-speed computer. The distribution of normal modes may be considerably altered according to the particular set of parameters from which it is calculated. Perhaps the nonuniqueness is a consequence of the fact that there are not enough data points (52) to sufficiently overdetermine the system of equations.[9]

Also, we would advance the suggestion that the pseudopotential technique, a method possessing a greater physical content than the harmonic approx-

TABLE VI. Beryllium: elastic constants (units of 10^{12} dyn/cm^2).

Elastic constant	Experimental[a]	Calculation A[b]	B	Equation[c] C
C_{11}	2.994	2.19 ± 0.10	2.55 ± 0.10	i
		2.19 ± 0.50	2.74 ± 0.49	$\frac{1}{2}$(ii + iv)
C_{12}	0.276	0.20 ± 0.41	0.15 ± 0.46	$\frac{1}{2}$(iv − ii)
		0.05 ± 0.30	0.09 ± 0.25	i − ii
		0.17 ± 0.32	0.16 ± 0.27	iv − i
C_{13}	0.110	0.10 ± 0.38	0.09 ± 0.25	v − vi
		0.05 ± 0.39	0.13 ± 0.24	v − iii
C_{33}	3.422	3.83 ± 0.20	3.84 ± 0.21	vii
C_{44}	1.662	1.41 ± 0.08	1.41 ± 0.08	vi
		1.59 ± 0.09	1.60 ± 0.10	iii

[a] From ultrasonic measurements (Ref. 8).

[b] Values in parentheses are taken from DWL and are not necessarily associated with equation numbers in column C.

[c] Equations (8) of Ref. 1 have been numbered i through vii in sequence.

imation and without the large numbers of adjustable parameters, may furnish a more satisfactory (and satisfying) approach.

Since this method allows for inclusion of specific interactions then data analysis using the technique might furnish a better understanding of the basic physical mechanisms operating in a metal. Attempts in this direction have recently been made for zinc[10] and beryllium,[10,11] with promising results.

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[1] R. E. DeWames, T. Wolfram, and G. W. Lehman, Phys. Rev. 138, A717 (1965).

[2] G. Borgonovi, G. Caglioti, and J. J. Antal, Phys. Rev. 132, 683 (1963).

[3] G. A. Alers and J. R. Neighbours, J. Phys. Chem. Solids 7, 58 (1958).

[4] R. A. Cowley, Proc. Phys. Soc. (London) 90, 1127 (1967).

[5] E. C. Svenssen and W. J. L. Buyers, Phys. Rev. 165, 1063 (1968).

[6] E. R. Cowley and R. A. Cowley, Proc. Roy. Soc. (London) A287, 259 (1965).

[7] R. E. Schmunk, R. M. Brugger, P. D. Randolph, and K. A. Strong, Phys. Rev. 128, 562 (1962).

[8] J. F. Smith and C. L. Arbogast, J. Appl. Phys. 31, 99 (1960).

[9] P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969), Chap. 11.

[10] E. G. Brovman, Yu. Kagan, and A. Kholas, Fiz. Tverd. Tela 11, 896 (1969) [Sov. Phys. Solid State 11, 733 (1969)].

[11] W. F. King, III and P. H. Cutler, Solid State Commun. 7, 295 (1969).

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Theory of Axially Symmetric O$^-$ Defect Centers in Alkali Halides

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An analysis is presented that permits a direct determination from electron-spin resonance (ESR) data of crystal-field splitting energies and also identifies which Kramers's doublet lies lowest for axially symmetric O$^-$ defect centers. The analysis is such as to make it unnecessary to solve the secular equation for both the crystal-field and spin-orbit interaction.

Electron-spin-resonance (ESR) absorption measurements made at 4.2 °K on alkali halide crystals subjected to electrolytic coloration followed by uv photolysis have demonstrated the existence of new paramagnetic centers. These centers have axial symmetry and are believed to be O$^-$ ions that substitute for halide ions.[1,2] The first theoretical analysis undertaken on the spectral parameters of this system is that due to Vannotti *et al.*[2,3] We would like to draw attention to two aspects of their analysis: (i) The energy of the $|P_z\rangle$ level given in Ref. 3 for the case of an orthorhombic crystal field [Eq. (5)] is not an exact root of the corresponding secular equation, a point which we shall discuss; (ii) it is difficult to establish the $|P\rangle$ energy-level sequence. In order to obtain this sequence, results due to Schoemaker and Boesman[4] were used.

In this paper, a mathematical procedure is developed which provides for exact solution to the crystal-field splitting energies of the aforementioned problem for ESR data, without any *a priori* assumption in regard to which Kramers's doublet lies lowest.

Under the combined action of an orthorhombic crystal field

$$\hat{\mathcal{H}}_{cf} = E[L_z^2 - \tfrac{1}{3}L(L+1)] + (\Delta/2)(L_x^2 - L_y^2) \qquad (1)$$

and the spin-orbit interaction

$$\hat{\mathcal{H}}_{LS} = \lambda \vec{L}\vec{S} . \qquad (2)$$

The energies of the three Kramers's doublets resulting from the $2p^5\text{-}{}^2P$ term of the free O$^-$ ion are given by

$$W^3 - (\tfrac{1}{3}E^2 + \tfrac{1}{4}\Delta^2 + \tfrac{3}{4}\lambda^2)W + \tfrac{2}{27}E^3 - \tfrac{1}{6}E\Delta^2 + \tfrac{1}{4}\lambda^3 = 0, \qquad (3)$$

and the corresponding eigenvectors take the form[5]