

Phonon Dispersion and Symmetry of Solid-J₂*

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The phonon dispersion curves, spectrum and specific heat of solid J₂ and Br₂ are calculated using a general central force parameter model, which is fitted to the available experimental data. The influence of the intramolecular degrees of freedom on the elastic constants and the compressibility is shown. The usefulness of group theoretical methods in the investigation of normal modes of vibrations in crystals is illustrated by applying them to the decomposition of the dynamical matrix.

1. Introduction

In the present paper the phonon dispersion curves for solid J₂ are determined within a central force model. The analogous calculations were done for Br₂ but the results are not given here. Former attempts with a Lennard-Jones-potential as an empirical potential function taking into account the polarizability of the dumbbell molecules could not explain the infrared data satisfactorily [1]. Further it is not sufficient to consider additional quadrupole interactions alone. One must ultimately pay regard to covalent intermolecular bonding. The phonon dispersion curves are calculated in the harmonic approximation for the symmetry directions Σ , Δ , Λ and $H' \rightarrow K$ of the Brillouin Zone (BZ)

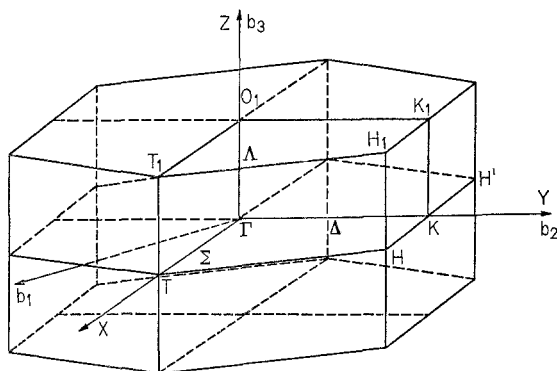


Fig. 1. First Brillouin Zone of the J₂-crystal

* Extract from a dissertation (D 26), Gießen.

(Fig. 1). The classification follows in terms of the irreducible multiplier representations (IMR) of the point group of the wave vector \mathbf{k} , called $G_{0\mathbf{k}}$. Some directions of symmetry can be completely factorized by group theory. The same projection technique is used in the calculation of the elastic constants and the compressibility in order to have simpler analytic expressions in the investigation of these quantities in the non-rigid-molecular model as well as in the rigid-molecular lattice.

The eigenvectors (EV) for the vibrations in the long wave limit and the geometry of the lattice are given in [1]. The crystal structure of iodine belongs to the space group $Cmca$ (D_{2h}^{18}).

2. Symmetry of the Dynamical Matrix and Its Eigenvectors

The relevance of symmetry to simplification of physical problems is of great importance. For example the translational invariance of the equations of motion in the Born-von-Karman theory implies, that the solutions transform according to the irreducible representations of the translation group. This fact reduces the problem of crystal vibrations to the solution of a $3r$ -dimensional eigenvalue problem, where r is the number of atoms per unit cell. The matrix of this problem is the so called dynamical matrix $\mathbf{t}(\mathbf{k})$.

$$t_{ij}^{\mu\nu}(\mathbf{k}) = (M_\mu M_\nu)^{-1/2} \sum_{\mathbf{h}} \phi_{ij}^{\mathbf{0}\mathbf{h}\mu\nu} \exp[i(\mathbf{k}, \mathbf{R}^{\mathbf{h}})]. \quad (1)$$

\mathbf{k} is the wave vector, M_μ is the mass of the atom at site μ , and $\phi_{ij}^{\mathbf{0}\mathbf{h}\mu\nu}$ is the force tensor between atoms at sites $(\mathbf{0}\mu)$ and $(\mathbf{h}\nu)$, $\mathbf{t}(\mathbf{k})$ is in our case a Hermitian matrix of dimension 12×12 . In terms of its EVs $\{e_k^{(j)}\}$ and corresponding eigenfrequencies (EF) $\{\omega^{(j)}(\mathbf{k})\}$ the atomic displacements may be written as

$$u_i^m = (M_\mu)^{-1/2} e_k^{(j)} e_i^m \exp\{i[(\mathbf{k}, \mathbf{R}^m) - \omega^{(j)}(\mathbf{k})t]\}. \quad (2)$$

Let the crystal be subjected to a symmetry operation of the space group $G: \{(\alpha|\mathbf{a}) := (\alpha|\mathbf{R}^{\mathbf{h}} + \mathbf{v}_\alpha)\}$, with α as an orthogonal transformation, $\mathbf{R}^{\mathbf{h}}$ as a primitive translation and \mathbf{v}_α as a non-primitive translation, which is unique for each α . The EVs then transform according to [2]

$$e_{\alpha\mathbf{k}}^{(j)} = \mathbf{O}(\mathbf{k}, \{\alpha|\mathbf{R}^{\mathbf{h}} + \mathbf{v}_\alpha\}) e_{\mathbf{k}}^{(j)}. \quad (3)$$

\mathbf{O} operates in the vibration space $L(\mathbf{k})$, which can be factorized into a particle space $L_p(\mathbf{k})$ and an euclidean space $L_E(\mathbf{k})$.

$$L(\mathbf{k}) = L_p(\mathbf{k}) \times L_E(\mathbf{k}). \quad (4)$$

With respect to this partition the explicit form of O is given by the unitary operator [2]

$$O(k, \{\alpha | R^h + v_\alpha\})_{i's}^{\mu\nu} = \alpha_{i's} \delta(\mu, F(v\alpha)) \exp[i(k, \{\alpha | R^h + v_\alpha\}^{-1} R^\mu - R^\nu)]. \quad (5)$$

The δ -symbol expresses the fact, that particle ν is carried into μ by the operation $(\alpha | R^h + v_\alpha)$.

If we restrict ourselves to the following subgroup of G , the group of k , $G_k: \{(\alpha | a) | \alpha k = k + K(k, \alpha) \text{ and } (\alpha | a) \in G\}$, K : vector of the reciprocal lattice, we have the commutation rule

$$[O(k, \{\alpha | a\}), t(k)]_- = 0, \quad (6)$$

where $\{O(k, \{\alpha | a\})\}$ provides a $3r$ -dimensional unitary representation of G_k . Instead of dealing with G_k , we can use the purely rotational elements $\{R\}$ of G_k , which constitute the point group G_{0k} of k . With each $R \in G_{0k}$ we associate a matrix $O(k, R)$ by

$$O(k, R) = \exp[i(k, R^h + v_R)] O(k, \{R | R^h + v_R\}) \quad (7)$$

and prove, that $\{O(k, R)\}$ provides an unitary multiplier representation of G_{0k} [2]

$$O(k, R_i) O(k, R_j) = \phi(k, R_i, R_j) O(k, R_i R_j) \quad (8)$$

with

$$\phi(k, R_i, R_j) = \exp[i(k - R_i^{-1} k, v_{R_j})]. \quad (8a)$$

If k is in the interior of the BZ, or the space group is symmorphic, ϕ equals unity and we have an ordinary representation of G_{0k} . Only for some k on the surface of the BZ in the case of a non-symmorphic space group the representation can differ from an ordinary one. The IMR are tabulated in Kovalev's book and the irreducible representations of the space groups are given by Zak [3]. The relation

$$[O(k, R), t(k)]_- = 0 \quad (9)$$

holds also for the operators $\{O(k, R)\}$. Now the dynamical matrix $t(k)$ can be factorized by means of a similarity transformation with a matrix U_k . U_k can be determined with the help of the operators

$$P_{ik}^{(s)}(k) = (f_s/h) \sum_{R \in G_{0k}} \tau_{ik}^{(s)}(k, R)^* O(k, R), \quad (10)$$

$i, k = 1 \dots f_s$ (f_s = dimension of the IMR $\{\tau^{(s)}(k, R)\}$), $s = 1 \dots q$ (q = number of inequivalent IMR), $a = 1 \dots c_s$ (c_s = number of times the s -th IMR is contained in $\{O(k, R)\}$), h denotes the order of G_{0k} . The numbers c_s are given by standard methods [4].

$$c_s = h^{-1} \sum_{R \in G_{0k}} \chi(k, R) \chi^{(s)}(k, R)^* \quad (11)$$

with χ and $\chi^{(s)}$ as characters of $\{\mathbf{O}(\mathbf{k}, \mathbf{R})\}$ and $\{\tau^{(s)}(\mathbf{k}, \mathbf{R})\}$ respectively. By applying $P_{ii}^{(s)}(\mathbf{k})$ to an orthogonal basis of $L(\mathbf{k})$, we can project out c_s symmetry-adapted vectors $\{\mathbf{b}_k^{(s,a,i)}, a=1 \dots c_s\}$. The partners of these vectors may be generated by applying to them the operator $P_{ik}^{(s)}(\mathbf{k})$ with $i \neq k$. In practice this can be done by constructing an operator-table from Eq. (10). All these vectors can be orthonormalized and arranged lexicographically to form the matrix U_k , where all the vectors belonging to the same s and i are grouped together. Similarity transformation of $\mathbf{t}(\mathbf{k})$ by U_k gives the blockdiagonal matrix

$$\text{diag}_{(s,i)} \{\mathbf{t}(\mathbf{k})^{(s,i)}\} = U_k^+ \mathbf{t}(\mathbf{k}) U_k \quad (12)$$

that means, one has to solve the eigenvalue problem in the subspaces $L^{(s,i)}(\mathbf{k}) \subset L(\mathbf{k})$ of dimension c_s only. Every $EF \omega^{(s,a)}(\mathbf{k})$ is at least f_s -fold degenerate and we have f_s diagonal blocks, each of dimension c_s .

3. Model Calculations

As mentioned before van-der-Waals- and quadrupole interactions alone are not sufficient for solid J_2 and covalent bonding was not considered in [1]. But there is a specific interaction in solid J_2 and Br_2 between neighboring molecules, which arises from partial intermolecular covalent bonding and which causes different charge distribution of the molecule in the solid phase and in the gas phase. This leads for example to the fact, that the distances between nonbonded nearest neighbors and next nearest neighbors in the same ac -plane are smaller than nonbonded nearest neighbors in different ac -planes [1, 5].

In fitting the $B_{1u}^{(2',1)}$ - and $B_{3u}^{(4',2)}$ -modes this covalent bonding type requires the consideration of neighbors up to 9-th order in the coupling constants and gives rise to relatively great values (compared to van-der-Waals interaction alone) for the intermolecular spring constants f_2 and f_9 between the atoms $(1-4')$ and $(1-3'')$ [6, 7] (Fig. 2). Neighbors of order 10 and 11 turn out to be unessential. For the identification of EVs of Fig. 2 in [1] and the notation used in this paper we should notice the following changes: $O_1 \rightarrow B_{1u}^{(2',1)}$, $O_2 \rightarrow A_u$, $O_3 \rightarrow B_{3u}^{(4',2)}$, $L_4 \rightarrow B_{3g}$, $L_3 \rightarrow B_{1g}$, $L_2 \rightarrow A_g^{(1,2)}$, $L_1 \rightarrow B_{2g}^{(3,2)}$, $I_2 \rightarrow A_g^{(1,1)}$, $I_1 \rightarrow B_{2g}^{(3,1)}$ (see Fig. 4). The potential was further fitted to the internal vibration frequency and the reciprocal compressibility κ^{-1} . The fit to κ^{-1} gives relatively small values for the coupling between molecules of the *same* orientation in the lattice as opposed to the values of f_2 and f_9 (see parameter set A in the Appendix). On the other side the contribution of the covalent bonding is comparable to that in the directions of f_2 and f_9 [5], so that one could regard the experimental value of κ^{-1} as being to small. For this reason,

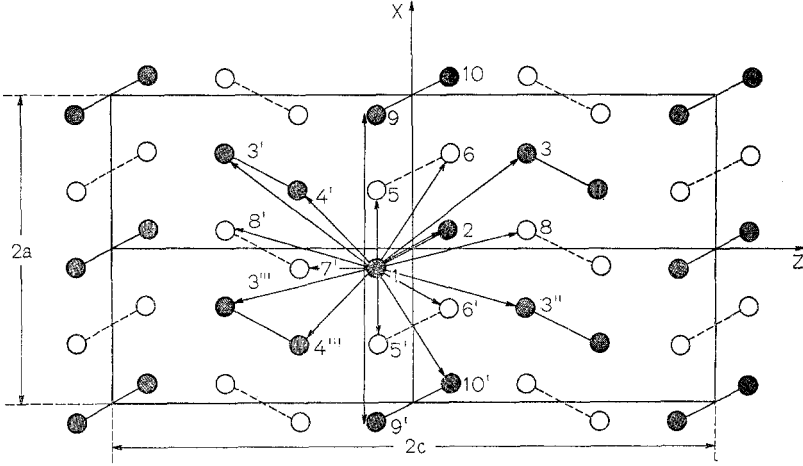


Fig. 2. J₂-lattice. The hatched particles belong to planes at distance $b/2$ below or above the drawing plane (ac -plane). The arrows represent couplings

besides the parameter set A , fitted to κ^{-1} , another set B is given, which is not in agreement with κ^{-1} , but which seems more realistic with respect to the coupling of molecules of the same orientation in one plane. At this point we want to remark, that for solid Br₂ the analogous calculations have been done, with the exception of a fit to κ^{-1} , because the experimental value of this is not known (see Table 1 in the Appendix).

The elastic constants and κ^{-1} for J₂ and Br₂ were investigated in the usual Born lattice theory as well as in the limit of an infinite intramolecular force constant. The elastic constants are given by [8, 9].

$$C_{ij,kl} = \hat{C}_{ik,jl} + \hat{C}_{jk,il} - \hat{C}_{ij,kl} + \sum_{\substack{m\mu \\ n\nu}} \hat{C}_{m,ij}^{\mu} R_{mn}^{\mu\nu} \hat{C}_{n,kl}^{\nu} \quad (13)$$

By means of the method developed in Chapter 2 the inhomogeneous part of the coefficient matrix (\hat{C}_{ij}) for the internal displacements of the sublattices of the crystal can be inverted in a blockdiagonal form, because this matrix commutes with the set of operators $\{\mathbf{O}(k=0, \mathbf{R}), \mathbf{R} \in G_0: \text{Point group of the crystal}\}$. The relevant matrix ($R_{mu}^{\mu\nu}$), which solves the problem and which can be derived from making use of the projector techniques mentioned above, has the form

$$R_{sr}^{\mu\nu} = \sum_{\substack{LK \\ \mu_1 j \\ \nu_1 i}} \mathbf{U}_{\Gamma s i}^{\mu \nu_1} \alpha_{i}^{\nu_1 (L)} (\mathbf{A}^{-1})_{LK} \alpha_{j}^{\mu_1 (K)} \mathbf{U}_{\Gamma j r}^{\mu_1 \nu} \quad (14)$$

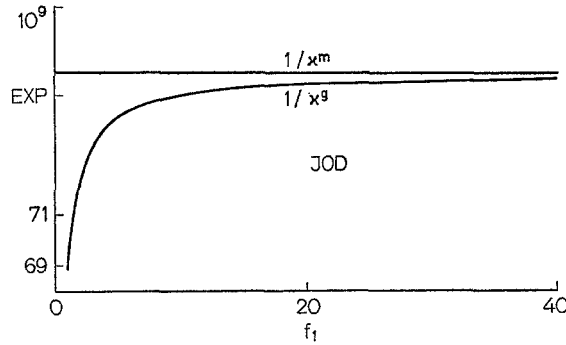


Fig. 3. Asymptotic curve for the reciprocal compressibility κ^{-1} . κ^{-1} in $\text{dyn} \cdot \text{cm}^{-2}$, f_1 in $10^4 \text{ dyn} \cdot \text{cm}^{-1}$. The zero-point is arbitrary

where

$$A_{LK} = \langle \alpha^{(L)} | \hat{C} | \alpha^{(K)} \rangle, \quad \hat{C} = U_T^+ \hat{C} U_T$$

with

$\{\alpha^{(L)}\}$: orthonormal set of vectors, orthogonal to the homogeneous solutions of \hat{C}

and

$$U_T := U_{k=0}.$$

In the rigid molecule approximation one must take the limit of infinite intramolecular force constant f_1 in Eq. (13). Fig. 3 shows the asymptotic curve of κ^{-1} (J_2 , parameter set A). This curve gives good agreement of the rigid molecule approximation with the usual theory in the actual range of intramolecular spring constant. Table 2 in the Appendix gives a comparison of the elastic constants and κ^{-1} in both approaches, Voigt notation is used.

Fig. 4 represents the phonon dispersion curves for parameter set A for solid J_2 in the direction of symmetry Σ , A , A and $H' \rightarrow K$. The notation is related to the BZ from Fig. 1. The classification of the bands follows according to the IMR of G_{0k} from the eigenvalue equation

$$t(\mathbf{k}) e_k^{(s, a, i)} = \omega^{(s, a)^2}(\mathbf{k}) e_k^{(s, a, i)} \tag{15}$$

and from the fact, that apart from accidental degeneracies the EVs corresponding to each eigenvalue of an operator transform irreducibly under the symmetry group of the operator, this means

$$O(\mathbf{k}, \mathbf{R}) e_k^{(s, a, i)} = \sum_{i'=1}^{f_s} \tau_{i'i}^{(s)}(\mathbf{k}, \mathbf{R}) e_k^{(s, a, i')}. \tag{16}$$

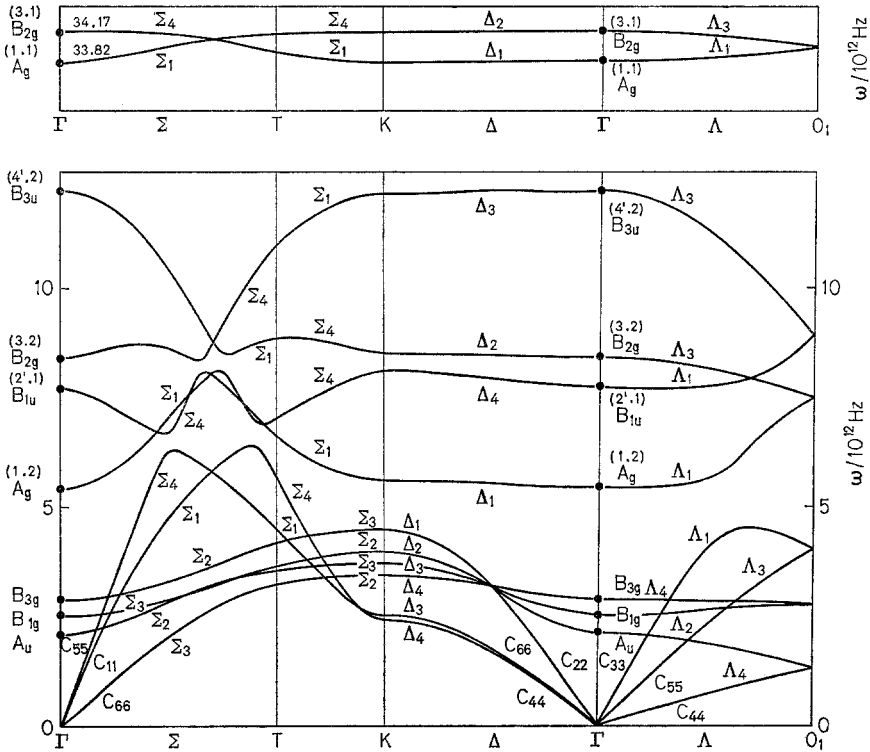


Fig. 4. Phonon dispersion curves of J_2 for parameter set A in the symmetry directions Σ , Δ , Λ and $H' \rightarrow K$. For the internal vibrations the zero-point is shifted arbitrarily

For the Γ -point the point group G_0 of the crystal is the important one and the classification can be done easily in terms of two character criteria for infrared active and raman active modes [10, 11]. The modes B_{1u} , B_{2u} and B_{3u} are infrared active and A_g , B_{1g} , B_{2g} and B_{3g} turn out to be raman active, while the A_u -mode is inactive.

The connection of branches of the dispersion relation is given by compatibility relations. For example if a symmetry line $\{k\}$ meets at a symmetry point k_0 , where $G_k \subset G_{k_0}$, then one can subduce with G_k from a given irreducible representation of G_{k_0} a representation of G_k , which has to be decomposed into its irreducible limit-representations ($k \rightarrow k_0$). This process involves the compatibility relations [12, 13]. One can easily establish these relations by using the known IMR and the decomposition formula (11). Besides the degeneracy caused by spatial symmetry time reversal can produce additional degeneracies of the dispersion curves [2, 13, 14]. The reason is essentially the following property of the

dynamical matrix:

$$t_{ij}^{\mu\nu}(\mathbf{k}) = t_{ij}^{\mu\nu}(-\mathbf{k})^* \quad (17)$$

If an element $\alpha_- \in G_0$ exists, such that $\alpha_- \mathbf{k} = -\mathbf{k}$, then we can form a new group $G_{0\mathbf{k}, -\mathbf{k}} = G_{0\mathbf{k}} + \alpha_- G_{0\mathbf{k}}$, in which $G_{0\mathbf{k}}$ is an invariant subgroup. We are able to show, that there are certain representations $\bar{O}(\mathbf{k}, \bar{\mathbf{R}})$, $\bar{\mathbf{R}} \in G_{0\mathbf{k}, -\mathbf{k}}$, which commute with $\mathbf{t}(\mathbf{k})$, where the representations of the coset $\alpha_- G_{0\mathbf{k}}$ are anti-unitary matrix operators [2].

Under some circumstances the enlarged number of symmetry elements produces additional degeneracies. In [2, 13] there is a character criterion to test every \mathbf{k} for additional degeneracy due to time reversal. In our case the points Γ , \mathbf{K} , T and the directions Σ , A and A' are not influenced (type 1 of the criterion), while the point O_1 has this additional degeneracy (type 3). We want to call special attention to the fact, that classification of the \mathbf{k} -points by time reversal sometimes reduces the expense of computation time very much.

As suggested from the crystal structure the frequencies at the Γ -point are very plausible. The intermolecular forces within the ac -layer will be greater than those between different layers, and therefore the vibrational frequencies of the in-plane motions are higher than those of the out-of-plane motions. This means that the frequencies of the $B_{1u}^{(2', 1)}$ -, $B_{3u}^{(4', 2)}$ -, $A_g^{(1, 2)}$ -, $B_{2g}^{(3, 2)}$ -modes and naturally the internal modes $A_g^{(1, 1)}$ and $B_{2g}^{(3, 1)}$ are higher than those of the A_u -, B_{1g} - and B_{3g} -modes. The frequency of $B_{3u}^{(4', 2)}$ is the highest external one, because this vibration involves the greatest change of the shortest intermolecular distance (EFs are given in Table 3 of the Appendix).

The values of the elastic constants C_{ik} , derived from the extrapolated gradients of the dispersion curves (Fig. 4) are in good agreement with the values calculated directly from relation (13).

The specific heat for constant volume is given by

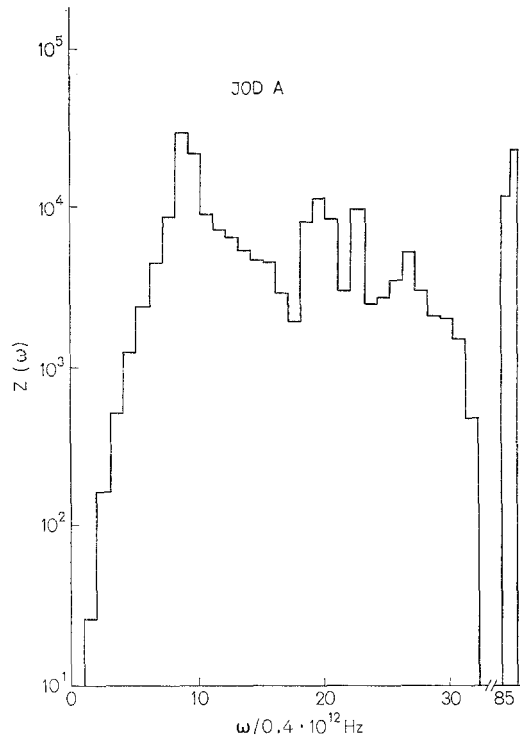
$$C_V = \left(\frac{\partial \langle E \rangle_T}{\partial T} \right)_V$$

with

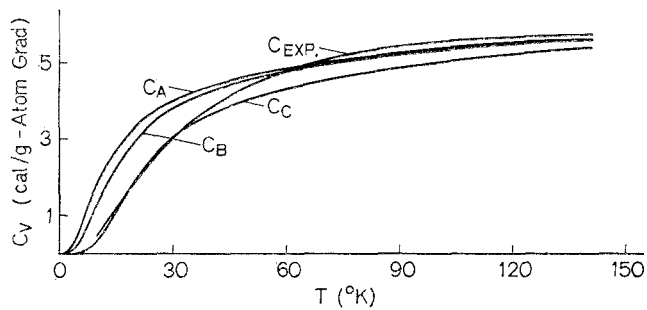
$$\begin{aligned} \langle E \rangle_T &= E_0 + \hbar \sum_{\mathbf{k}, \sigma} \langle n_{\sigma}(\mathbf{k}) \rangle_T \omega^{(\sigma)}(\mathbf{k}) \\ &= E_0 + \hbar \int_0^{\omega_{\max}} (\exp[\hbar \omega / k_B T] - 1)^{-1} \omega Z(\omega) d\omega \end{aligned}$$

E_0 = Zero-point energy, $\langle n_{\sigma}(\mathbf{k}) \rangle_T$ = Thermal phonon population number, $Z(\omega)$ = Phonon-spectrum.

$Z(\omega) d\omega$ ($d\omega \rightarrow 0$) denotes the number of EFs of the crystal within the interval $(\omega \dots \omega + d\omega)$. Using the root sampling method we can get an approximation for the phonon spectrum, which is illustrated



a



b

Fig. 5a and b. Histogram of the phonon spectrum approximation. $Z(\omega)$ is given in logarithmic scale while ω is linear (a). Specific heat of J₂ for several parameter sets (b)

in Fig. 5a in form of a histogram for the parameter set A of J_2 . For this purpose we calculate the corresponding EFs from Eq. (15) for a great number of homogeneously distributed k -vectors in the BZ (about 9000 k -points in the BZ were used). In order to have the best effectiveness as possible that means the greatest density of k -states for a given expense of calculation, we choose the elementary region of the BZ as the domain for the k -vectors weighting them according to the symmetry of the phonon bands. Numerical integration in the formula for C_V gives the specific heat of solid J_2 . Fig. 5b shows the specific heat curve for several parameter sets. Set C was introduced because set A does not reproduce the experimental data for C_V in the range of low temperature. Therefore in case C the gradients of the acoustic branches were enlarged by varying the parameters. Set C itself yields a too large value of κ^{-1} (see Appendix). It is however an open question how far the available experimental data for the specific heat are valid especially because the experiments are very old [15]. Further for set C there results a coupling between molecules of the same orientation respectively between molecules of different layers which seems to be too strong. Finally the parameter set B is a compromise for an eventual insecurity in measuring κ^{-1} or the specific heat respectively.

4. Appendix

The value for κ^{-1} in the case of parameter set C for J_2 is $1.61468 \cdot 10^{11}$ dyn \cdot cm $^{-2}$.

Table 1

Force constants between atoms (see Fig. 2) $\cdot 10^4$ dyn \cdot cm $^{-1}$	Parameter set		
	J_2		Br_2
	A	B	A
1-2: f_1	11.500	11.500	20.700
1-4': f_2	0.642	0.642	0.557
1-10': f_3	0.062	0.250	0.217
1-6': f_4	0.030	0.060	0.069
1-5: f_5	0.040	0.080	0.052
1-7': f_6	0.025	0.025	0.020
1-9: f_7	0.055	0.150	0.130
1-6: f_8	0.015	0.030	0.026
1-3''': f_9	0.422	0.422	0.343
1-8': f_{10}	0.010	0.010	0.010
1-3': f_{11}	0.010	0.010	0.010

Table 2

Elastic constants and κ^{-1} $\cdot 10^{11}$ dyn \cdot cm ⁻²	Parameter set				
	J ₂		Br ₂	J ₂	Br ₂
	A	B	A	A($f_1 = \infty$)	A($f_1 = \infty$)
C_{11}	0.76061	1.75537	1.77099	0.76600	1.78116
C_{12}	0.09855	0.19725	0.16342	0.09820	0.16271
C_{13}	0.82408	1.13544	1.13999	0.83869	1.15828
C_{66}	0.10247	0.20298	0.16890	0.10247	0.16890
C_{55}	1.04084	1.18572	1.13625	1.09896	1.16059
C_{22}	0.32678	0.58075	0.51155	0.32663	0.51158
C_{23}	0.08614	0.10666	0.11265	0.08518	0.11138
C_{44}	0.09486	0.10836	0.10366	0.09486	0.10366
C_{33}	3.70798	3.94544	3.50209	3.74799	3.53489
κ^{-1}	0.75698	1.01781	0.95742	0.76498	0.96582

The force-constant tensors given here complete the tensors introduced in [1] for the extended model of this paper. The connection between the force-constant tensor elements and the springs follows from the geometry of the lattice (Fig. 2) and Table 1 in [1]. The limiting frequencies for the Γ -point are the following. $\lambda^{(s,a)}(\mathbf{k}) := m(\omega^{(s,a)}(\mathbf{k}))^2$ by definition.

Table 3

Eigenfrequencies for the $\mathbf{k} = \mathbf{0}$ -motion 10^{13} Hz	Parameter set			Force-constant tensors
	J ₂	Br ₂	A	
	A	B	A	
$A_g^{(1,1)}$	3.3820	3.3850	5.6535	1-9: $\begin{Bmatrix} \beta_7 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{Bmatrix}$
$A_g^{(1,2)}$	0.5416	0.6977	0.8276	1-6: $\begin{Bmatrix} \gamma_8 & -\varepsilon_8 & \zeta_8 \\ -\varepsilon_8 & \alpha_8 & -\delta_8 \\ \zeta_8 & -\delta_8 & \beta_8 \end{Bmatrix}$
B_{1g}	0.2513	0.3369	0.4459	1-3''': $\begin{Bmatrix} \beta_9 & 0 & -\delta_9 \\ 0 & 0 & 0 \\ -\delta_9 & 0 & \alpha_9 \end{Bmatrix}$
$B_{2g}^{(3,1)}$	3.4168	3.4200	5.6763	1-8': $\begin{Bmatrix} \gamma_{10} & \varepsilon_{10} & -\zeta_{10} \\ \varepsilon_{10} & \alpha_{10} & -\delta_{10} \\ -\zeta_{10} & -\delta_{10} & \beta_{10} \end{Bmatrix}$
$B_{2g}^{(3,2)}$	0.8385	0.9470	1.1077	1-3': $\begin{Bmatrix} \beta_{11} & 0 & -\delta_{11} \\ 0 & 0 & 0 \\ -\delta_{11} & 0 & \alpha_{11} \end{Bmatrix}$
B_{3g}	0.2856	0.3633	0.4659	
A_u	0.2096	0.2096	0.2465	
$B_{1u}^{(2',1)}$	0.7700	0.7700	0.9200	
$B_{1u}^{(2',2)}$	0	0	0	
B_{2u}	0	0	0	
$B_{3u}^{(4',1)}$	0	0	0	
$B_{3u}^{(4',2)}$	1.2200	1.2200	1.400	

$$B_{1g}: \lambda^{(2,1)}(\Gamma) = -4\{\alpha_4 + \alpha_8 + 2\alpha_{10}\}$$

$$B_{3g}: \lambda^{(4,1)}(\Gamma) = -4\{\alpha_4 + \alpha_6 + \alpha_8\}$$

$$A_u: \lambda^{(1',1)}(\Gamma) = -4\{\alpha_6 + 2\alpha_{10}\}$$

$$B_{1u}: \lambda^{(2',1)}(\Gamma) = -4\{\beta_2 + \beta_9 + 2\gamma_{10} + \beta_{11}\}$$

$$B_{3u}: \lambda^{(4',2)}(\Gamma) = -4\{\alpha_2 + \beta_6 + \alpha_9 + 2\beta_{10} + \alpha_{11}\},$$

$$A_g: \begin{aligned} \lambda^{(1,1)}(\Gamma) &= D'' + F'' \pm ((D'' - F'')^2 + 4B''^2)^{1/2} \\ \lambda^{(1,2)}(\Gamma) &= D'' + F'' \pm ((D'' - F'')^2 + 4B''^2)^{1/2} \end{aligned}$$

$$B_{2g}: \begin{aligned} \lambda^{(3,1)}(\Gamma) &= A'' + C'' \pm ((A'' - C'')^2 + 4B''^2)^{1/2}, \\ \lambda^{(3,2)}(\Gamma) &= A'' + C'' \pm ((A'' - C'')^2 + 4B''^2)^{1/2}, \end{aligned}$$

$$A'' = -\{\beta_1 + 2\beta_2 + \alpha_3 + 2\gamma_4 + 2\gamma_8\}$$

$$B'' = -\{\delta_1 + \delta_3 + 2\zeta_4 + 2\zeta_8\}$$

$$C'' = -\{\alpha_1 + \beta_3 + 2\beta_4 + 2\beta_8 + 2\alpha_9 + 4\beta_{10} + 2\alpha_{11}\}$$

$$D'' = -\{\beta_1 + \alpha_3 + 2\gamma_4 + 2\gamma_8 + 2\beta_9 + 4\gamma_{10} + 2\beta_{11}\}$$

$$F'' = -\{\alpha_1 + 2\alpha_2 + \beta_3 + 2\beta_4 + 2\beta_6 + 2\beta_8\}.$$

The reduction for the A and Σ -direction in k -space involves 2-dimensional partial problems with the solutions

$L^{(2)}(A)$:

$$\begin{aligned} \lambda_{1,2}^{(2)} &= -2 \left\{ \alpha_4 + \alpha_6 + \alpha_8 + 2\alpha_{10} + 2\alpha_{10} \cos \left(k_z \frac{c}{2} \right) \right\} \\ &\mp 2 \left((\alpha_4 + \alpha_8)^2 + \alpha_6^2 - 2(\alpha_4 + \alpha_8)\alpha_6 \cos \left(k_z \frac{c}{2} \right) \right)^{1/2}. \end{aligned}$$

$L^{(4)}(A)$:

$$\begin{aligned} \lambda_{1,2}^{(4)} &= -2 \left\{ \alpha_4 + \alpha_6 + \alpha_8 + 2\alpha_{10} - 2\alpha_{10} \cos \left(k_z \frac{c}{2} \right) \right\} \\ &\mp 2 \left((\alpha_4 + \alpha_8)^2 + \alpha_6^2 + 2(\alpha_4 + \alpha_8)\alpha_6 \cos \left(k_z \frac{c}{2} \right) \right)^{1/2}. \end{aligned}$$

L⁽²⁾(Σ):

$$\begin{aligned} \lambda_{1,2}^{(2)} = & -2\{\alpha_4 + 2\alpha_5 + 2\alpha_6 + \alpha_8 + 2\alpha_{10}\} + 4\alpha_5 \cos\left(k_x \frac{a}{2}\right) \\ & \pm 2\left(\alpha_4^2 + \alpha_8^2 + 4\alpha_{10}^2 + 2\alpha_4 \alpha_8 \cos(k_x a) \right. \\ & \left. - 4\alpha_{10}(\alpha_4 + \alpha_8) \cos\left(k_x \frac{a}{2}\right)\right)^{1/2}. \end{aligned}$$

L⁽³⁾(Σ):

$$\begin{aligned} \lambda_{1,2}^{(3)} = & -2\{\alpha_4 + 2\alpha_5 + \alpha_8 + 2\alpha_{10}\} + 4\alpha_5 \cos\left(k_x \frac{a}{2}\right) \\ & \pm 2\left(\alpha_4^2 + \alpha_8^2 + 4\alpha_{10}^2 + 2\alpha_4 \alpha_8 \cos(k_x a) \right. \\ & \left. + 4\alpha_{10}(\alpha_4 + \alpha_8) \cos\left(k_x \frac{a}{2}\right)\right)^{1/2}. \end{aligned}$$

The calculations were performed on the IBM 7094 of the DRZ Darmstadt and on the CD 3300 of the University of Gießen. I am very grateful for helpful discussions with Prof. Dr. W. Ludwig, TH Darmstadt and for some valuable remarks of Prof. J. Zak, Technion-Israel Institute of Technology, Haifa.

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