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ROLE OF THREE-BODY FORCES IN THE DYNAMICAL PROPERTIES OF WHITE TIN

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ROLE OF THREE-BODY FORCES IN THE DYNAMICAL PROPERTIES OF WHITE TIN

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Summary

Elastic characteristics of white tin are investigated taking into account the presence of three-body interactions between the ions. The calculation shows that three-body noncentral forces contribute substantially to the elastic moduli and to one of the optical frequencies.

Резюме

Анализируются упругие свойства белого олова учитывая наличие трехчастичного взаимодействия между ионами. Расчеты показывают, что вклады непарных трехчастичных сил в модули упругости и в одну из оптических частот являются существенными.

Covalent forces between the ions are expected to play an important role in determining physical properties of some metals. In particular, they seem to be responsible for stabilizing complex crystal structures. The origine of these forces can be seen if one considers the power series expansion of the binding energy in terms of the electron-ion pseudopotential, where terms describing noncentral many-body interactions appear beyond second order [1][2] . For the study of effects connected with many-body forces the case of white tin was chosen, for which previous investigations [1] of the phonon dispersion curves indicate the presence of covalent forces. The present results for binding energy, three elastic moduli and one of the optical frequencies, contain contributions from three-body forces, too. In the a priori calculation of 3-d order terms the point was rather to analyze their relative contributions to the physical characteristics; while finding an optimum agreement with all experimental data was postponed to a later stage.

Thus, instead of introducing a multiparametrical model, the very simple pseudopotential of the form [3]*

$$V(q) = \frac{8\pi Z}{\Omega}\left\{-\frac{\cos q\, r_c}{q^2} + \beta\,.\lambda\,(q)\right\} \qquad /1/$$

was used in our calculations. Here Ω is the atomic volume, Z is the ionic charge, the function $\lambda(q)$ cuts off shortly beyond zero vanishing at any other reciprocal lattice vector. The parameter β was determined by the condition of zero pressure at the experimental value of Ω . The zero of the pseudopotential was adjusted by varying the effective core radius r_c. For convergency a damping factor usually assumed [4] multiplying /1/ was also included. The binding energy per atom as a function of the tetragonal ratio $\gamma = c/a$ and the atomic volume Ω has then the form

$$E = E^{(0)}(\Omega) - \frac{4Z^2 M(\gamma)}{\Omega^{1/3}} + \frac{b}{\Omega} + E^{(2)}(\Omega,\gamma) + E^{(3)}(\Omega,\gamma) + \ldots\ldots \qquad /2/$$

Here $b = 8\pi Z\left(\frac{r_c^2}{2} + \beta\right)$ and the different contributions are the energy of the homogeneous electron liquid [5] , the Coulomb energy of the system of point ions with a γ -dependent Madelung constant, the energy arising from the zeroth Fourier coefficient of the non-coulombic part of electron-ion interaction and finally the band structure terms of 2-nd, 3-d.... order in V . Of these latters one considers usually [3] only

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* Atomic units are used except that energy is given in rydbergs.

$$E^{(2)} = -\Omega/2 \sum_{\underline{G}} \frac{G^2}{4\pi} |v(\underline{G})|^2 \left(1 - 1/\varepsilon(\underline{G})\right) \qquad /3/$$

describing the pair interaction of charged ions via the polarized electron liquid. Here $v(\underline{G})$ stands for $V(G)$ multiplied by the form factor of the unit cell, ε is the static dielectric function, and the sum is over all $\underline{G}$ vectors of the reciprocal lattice.

The next term involves the interaction energies within different sets of any three atoms [1][2] and has the form

$$E^{(3)} = -\Omega \sum_{\underline{G}} \sum_{\underline{G}'} \frac{v(\underline{G})}{\varepsilon(\underline{G})} \frac{v(\underline{G}')}{\varepsilon(\underline{G}')} \frac{v(\underline{G}'-\underline{G})}{\varepsilon(\underline{G}'-\underline{G})} \Gamma^{(3)}\left(\underline{G}, -G', \underline{G}'-\underline{G}\right) \qquad /4/$$

where $\Gamma^{(3)}$ is the full 3-d order polarization diagram of the electron liquid [1][2][6]. /Recently [7] the same expression was used in an effective Hamiltonian approach of the band structure energy./

In the numerical calculations the free-electron approximation for $\Gamma^{(3)}$ has been used [6].

Besides the binding energy the bulk modulus* B and the shear moduli C and C' defined by

$$B = \Omega \frac{\partial^2 E}{\partial \Omega^2} = \frac{2}{9}\left(c_{11} + c_{12} + \frac{1}{2} c_{33} + 2c_{13}\right)$$

$$C = \gamma^2 \frac{\partial^2 E}{\partial \gamma^2} = \frac{2}{9}\left(c_{11} + c_{12} + 2c_{33} - 4c_{13}\right)$$

$$C' = -\gamma \frac{\partial^2 E}{\partial \Omega \partial \gamma} = \frac{2}{9}\left(c_{11} + c_{12} - c_{33} - c_{13}\right)$$

were calculated. For tetragonal tin one has [8] $\Omega = 179.937$ a.u. and $\gamma = 0.543273$. The value of r_c at which V/ε follows closely the potential of Heine and Abarenkov [4] is about 1.12 a.u. The results of our calculations are summarized in the table for three values of the core radius parameter r_c. The experimental value of the binding energy, which, as defined here, equals to the sum of the first four atomic ionization potentials and the observed sublimation heat 0.23 ry is seen to lie between two calculated values. It is to be noted, that 3-d order terms contribute to the binding energy by an order of magnitude less than those of 2-d order.

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*For complex lattice structures like that of white tin B is obviously not the inverse hydrostatic compressibility. It is to be noted also that such a "static" way of determining elastic moduli involving 3-d power of v in /2/ corresponds [9][10] to accounting for terms up to 5-th order in the method of long waves.

The picture is, however, quite different in the case of the dynamical properties connected with energy derivatives, where the 3-d order contribution is mostly on the same scale as the usual 2-nd order band structure terms. One has, in addition, a considerable cancellation of the other terms resulting in the fact, that the 3-d order contribution is substantial in the final results for all the three moduli B, C and C'. Though a more flexible potential is necessary to reproduce with better accuracy the experimental values, the present results covering a fairly wide range of r_c clearly show the importance of three-body interactions in the calculation of the elastic properties.

The contribution from three-body forces is apparent also in the value of the longitudinal optical frequency at zero wave vector. Our calculations showed that restricting oneself to central pair interactions ω_{Lo}^2 cannot be even approximately reproduced by any choice of the model potential, the second order result being always close to $0.32\times10^{24}/s^2$ in contrast with the observed $1.98\times10^{24}/s^2$. Now, including 3-d order terms one gets the much better value $2.46\times10^{24}/s^2$. This frequency is therefore highly sensitive to the covalent character of the interactions, a situation similar to the problem of gap parameters in the case of some semiconductors [11]. We think that analogous considerations apply also to the case of some other metals, like zinc or lead, as suggested previously [12] [13] and to some recent calculations of the elastic moduli for hexagonal metals [14]. A more detailed calculation of the dynamical characteristics is under progress.

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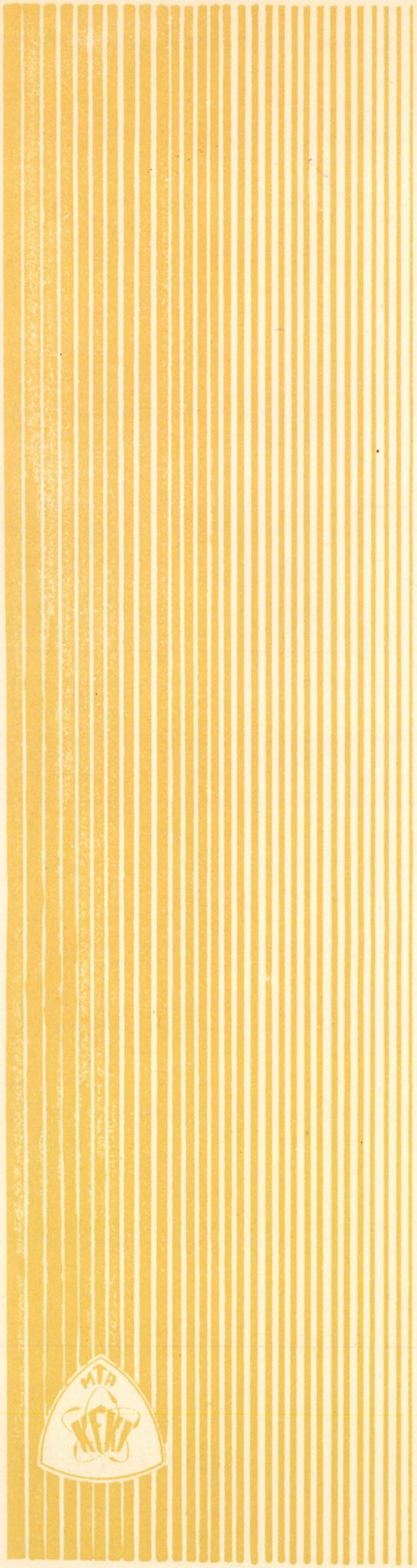
Table caption

Binding energy and elastic properties of white tin. Energy is given in rydbergs, all other quantities in 10^{11} dyn/cm^2. The different contributions are discussed in the text. The rows labelled by a, b, c are results for r_c=1.03, 1.10, 1.17 a.u., respectively.

	electronic	coulomb	electron-ion noncoulombic 1-st order	band structure 2-nd order	band structure 3-d order	total	experimental [8]
E	-0.207	-8.101	a 1.668 b 1.843 c 1.830	-0.482 -0.410 -0.385	-0.013 -0.015 -0.0001	-7.135 -6.890 -6.863	-6.98
$\rho = -\frac{\partial E}{\partial \Omega}$	5.032	-22.074	a 13.603 b 15.029 c 14.882	3.549 1.833 -0.120	-0.110 0.180 1.280	0	0
$\rho' = \frac{1}{\Omega} \gamma \frac{\partial E}{\partial \gamma}$	0	-0.063	a b 0 c	0.059 0.137 0.198	-0.041 -0.151 -0.286	-0.044 -0.072 -0.151	0
$B = \Omega \frac{\partial^2 E}{\partial \Omega^2}$	10.121	-29.432	a 27.200 b 30.058 c 29.764	-3.588 -7.305 -11.102	-0.780 3.643 8.997	3.521 7.005 8.348	5.79
$C = \gamma^2 \frac{1}{\Omega} \frac{\gamma^2 E}{\partial \gamma^2}$	0	26.738	a b 0 c	-25.760 -24.801 -23.210	1.210 -0.626 -1.973	2.188 1.311 1.555	4.66
$C' = \gamma \frac{\partial^2 E}{\partial \Omega \partial \gamma}$	0	0.021	a b 0 c	-0.285 -0.430 -0.604	0.477 0.657 0.820	0.213 0.248 0.237	-0.075

01.854



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