

## The softening of crystals due to interacting Jahn-Teller impurities

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 631

(<http://iopscience.iop.org/0953-8984/3/6/001>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 11/05/2010 at 07:05

Please note that [terms and conditions apply](#).

# The softening of crystals due to interacting Jahn–Teller impurities

G I Bersuker and A O Solonenko

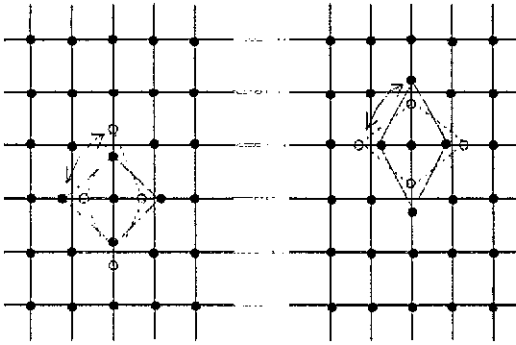
Institute of Chemistry, Academy of Sciences of Moldavian SSR, Kishinev 277028, USSR

Received 19 June 1990, in final form 28 September 1990

**Abstract.** The dynamics in a system of impurity centres with a two-fold orbitally degenerate electronic state strongly coupled to the appropriate crystalline vibrations are investigated. The interaction between impurities occurs via the same phonons as participate in the electron–phonon coupling. A novel type of motion is shown to appear in the system owing to the interdependent reorientations of the centres between their energetically equivalent nuclear configurations. The influence of the interacting impurities on the elastic properties of the crystal is discussed.

## 1. Introduction

Of the different types of impurity centre a special class is formed by impurities with degenerate electronic states which possess some specific features due to the Jahn–Teller effect (JTE) (Englman 1972, Bersuker and Polinger 1989). The theoretical aspects of the situation with different types of single Jahn–Teller ( $JT$ ) ion were discussed thoroughly. On the other hand the cooperative phenomena in crystals in which  $JT$  ions form regular sublattices and strongly interact between themselves have also been investigated rather well (Gehring and Gehring 1975). Much less attention has been paid to the cases which are in between these two cases, i.e. when the concentration of the impurities is high enough that the  $JT$  ions cannot be treated as single ions but on the other hand it is low enough that it is possible to consider the interaction of the given centre with only one nearest  $JT$  impurity as the strongest effect. By the term ‘interaction’ hereafter, we shall mean the interaction via the vibrations of the host crystal since the impurities are assumed to be separated by several lattice cells. In fact the degeneracy of the electronic states of the impurity indicates the presence of several energetically equivalent distributions of localized electronic cloud and, consequently, owing to the electron–phonon interaction, of several energetically equivalent nuclear configurations of the surrounding lattice. Hence, reorientation of the system between these configurations can occur (figure 1). This reorientation at a single centre induces a wave of lattice deformations around the impurity which can affect the reorientation of the other  $JT$  centre, and vice versa. So the centres have to reorient interdependently, and this new type of motion in the system results in a novel energy spectrum of localized vibronic states. This intercentre interaction will be called the angular interaction. There is another possibility for interimpurity interaction. The coupling of the electronic state of the impurity with the non-totally



**Figure 1.** Schematic illustration of impurity centres in degenerate electronic states taking into account their interaction with the near-neighbour crystalline environment. (For simplicity, the cross-section of the simple cubic lattice is presented.) The full and broken rhombi correspond to the deformations of the impurity centres along different tetrahedral axes (the localization of impurity centres in different energetically equivalent minima of the adiabatic potential). The reorientations of the impurity centres between the equivalent nuclear configurations, resulting in the angular interaction between the centres, are shown by arrows.

symmetric crystalline vibrations deforms the surrounding lattice and thus induces minima on the surface of the adiabatic potential. This means that the nuclei of the crystal are displaced from their lattice points, their frequencies being changed. These displacements induce the appropriate deformation in the nearest surroundings of the other centre. Hence in this case also the distortions at both centres occur interdependently. This type of interaction between the centres (we shall call it the radial interaction) forms a new density of crystalline vibrations. The reorientational motion can be considered as slow compared with all the other vibrational degrees of freedom in the impurity crystal. This enables one to separate the angular and radial interactions within the adiabatic approximation.

Thus, if an experiment which deals with localized states is discussed, one has to take into account the angular interaction between the JT ions first of all. When the data on the density of phonon states or on the fields of strains induced by the impurities are of interest, the radial interaction should be considered.

In the present paper we discuss the influence of the JT impurities on the elastic properties of the crystals (EPR, infrared and Raman spectra, and magnetic susceptibility will be considered in forthcoming papers). The softening of the crystal (the reduction in some elastic moduli) is due to the ability of the system to reorient between the equivalent configurations. This means that the elasticity of the crystal with respect to the external deformations of appropriate symmetry (corresponding to the elasticity with respect to energetically equivalent distortions of the impurity surroundings) is reduced. Experimentally the effect of softening has been reported to have been observed in a GaAs crystal doped with Cu (Averkiev, Ashirov, Gutkin, Osipov and Sedov 1986). When the concentration of the impurities increases, the interaction between them increases too and the reorientational dynamics of the interacting centres become complicated to a large degree. This can affect essentially the appropriate elasticity coefficients. In the present work the influence of the intercentre interaction on the softening of the crystal due to the impurity centres with twofold orbitally degenerate electronic states in the case of strong vibronic coupling is discussed. The dependences of the elasticity modulus

on the interimpurity distances, as well as on the temperature and the external strain are obtained.

## 2. Non-interacting impurities

In this section we discuss the influence of the JT impurities on the elastic properties of crystals in the case of small impurity concentrations when one can neglect the interaction between the JT centres. For a centre in the twofold orbitally degenerate electronic state interacting with an  $E$ -type vibration of the immediate neighbours and strain the Hamiltonian has the form (Bersuker and Polinger 1989)

$$H = H_0 + H_{\text{vib}} + H_{\text{cldef}} \quad (1)$$

where

$$\begin{aligned} H_0 &= -\frac{\hbar^2}{2} \sum_{\gamma=\theta,\epsilon} \frac{\partial^2}{\partial Q_{E_\gamma}^2} + \frac{\omega_E^2}{2} \sum_{\gamma=\theta,\epsilon} Q_{E_\gamma}^2 \\ H_{\text{vib}} &= V_E \sum_{\gamma=\theta,\epsilon} Q_{E_\gamma} \hat{\mathbf{C}}_{E_\gamma} \\ H_{\text{strain}} &= b \sum_{\gamma=\theta,\epsilon} \varepsilon_\gamma \hat{\mathbf{C}}_{E_\gamma}. \end{aligned} \quad (2)$$

The Hamiltonian (2) is written within the approximation of the linear vibronic  $H_{\text{vib}}$  and electron–strain  $H_{\text{strain}}$  couplings.  $H_0$  is the Hamiltonian describing the  $E$ -type harmonic vibrations of the immediate neighbours,  $Q_{E_\gamma}$  being their symmetrized displacements.  $V_E$  is the constant of linear vibronic interaction,  $\hat{\mathbf{C}}_{E_\gamma}$  are the electronic matrices in the basis of the electronic  $E$  states  $\psi_{\pm}$  of the impurity (Bersuker and Polinger 1989) ( $\hat{\mathbf{C}}_{E_\delta} = \sigma_x$  and  $\hat{\mathbf{C}}_{E_\epsilon} = \sigma_y$ , where  $\sigma_x$  and  $\sigma_y$  are the Pauli matrices).  $b$  is the constant of the electron–strain interaction,  $\varepsilon_\gamma$  are symmetrized combinations of the components  $e_{ij}$  of the strain tensor, transforming after the row  $\gamma$  of the irreducible representation  $E$  of the point symmetry of the impurity centre ( $\varepsilon_\delta = e_{zz} - (e_{xx} + e_{yy})/2$ ;  $\varepsilon_\epsilon = (e_{xx} - e_{yy})/\sqrt{3}/2$ ). In the case of strong linear vibronic coupling under consideration the splitting of the degenerate electronic state by the vibronic interaction is large enough to restrict the consideration by the low sheet of the adiabatic potential of the system, the latter being obtained as a result of the diagonalization of the Hamiltonian  $H_0 + H_{\text{vib}}$ . The operator  $S$  transforming the Hamiltonian to its diagonal form is as follows:

$$\hat{S} = \frac{1}{\sqrt{2}} \begin{pmatrix} \exp(-i\varphi/2) & \exp(-i\varphi/2) \\ \exp(i\varphi/2) & -\exp(i\varphi/2) \end{pmatrix} \quad (3)$$

where  $\varphi = \tan^{-1}(Q_{E_\epsilon}/Q_{E_\delta})$ . In this case the adiabatic electronic function corresponding to this lower sheet is of the form

$$\psi_{\text{ad}} = (1/\sqrt{2})[\exp(-i\varphi/2)\psi_+(r) - \exp(i\varphi/2)\psi_-(r)]. \quad (4)$$

Here  $r$  is the electronic variable. When the deformations are not too strong ( $b\varepsilon_\gamma \ll E_{JT}$ ) the electron–strain interaction can be considered in the frame of the perturbation theory,

neglecting the mixing of the different sheets of the adiabatic potential. For the states of the lower sheet in the first-order perturbation theory, one has

$$\overline{H_{\text{strain}}} = \langle \psi_{\text{ad}} | H_{\text{strain}} | \psi_{\text{ad}} \rangle = -b(\varepsilon_{\theta} \cos \varphi + \varepsilon_{\varepsilon} \sin \varphi). \quad (5)$$

Thus the final Hamiltonian of the system has the following form:

$$H = -(\hbar^2/2)(\partial^2/\partial\rho^2) + (\hbar^2/2\rho^2)L_{\varphi}^2 + \frac{1}{2}\omega_E^2\rho^2 - V_E\rho - b \times (\varepsilon_{\theta} \cos \varphi + \varepsilon_{\varepsilon} \sin \varphi). \quad (6)$$

In equation (6) the wavefunction is replaced in accordance with the relations  $\Psi = \Phi/\sqrt{\rho}$ ,  $\rho = (Q_{E_{\delta}}^2 + Q_{E_{\varepsilon}}^2)^{1/2}$  and  $L_{\varphi} = -i\partial/\partial\varphi$ .

In the absence of external strain the adiabatic potential of the system is known to possess an equipotential continuum of minima (the trough) along variable  $\varphi$ , and the energy spectrum is a superposition of the spectrum of harmonic vibrations along  $\rho$  near the new equilibrium positions  $\rho_0 = |V_E|/\omega_E^2$  and of the spectrum of rotations along the angular variable  $\varphi$  with half-integer quantum numbers of the angular momentum  $l_{\varphi} = \pm\frac{1}{2}, \pm\frac{3}{2}, \dots$ . The external strain cannot affect the vibrations along  $\rho$  but it deforms the trough, and consequently the vibronic states of the rotational spectrum are split. If the external strain is strong enough, the system can be localized near the minima that corresponds to the distorted nuclear configuration.

The change in the elasticity modulus of the crystal induced by the vibronic coupling of the impurity electrons with the crystalline vibrations can be written as follows (Leibfried 1955):

$$\Delta(C_{11} - C_{12}) = \frac{2}{3}(\partial^2 F/\partial\varepsilon_{\theta}^2) \quad (7)$$

where  $F$  is the contribution of the impurity centre to the free energy of the crystal  $F = E - kT \ln Z$ ;  $Z$  is a statistical sum over the vibronic states of the centre. To simplify (7) the strain is assumed to be applied along the  $\langle 100 \rangle$  direction only;  $\varepsilon_{\varepsilon} = 0$ ,  $\varepsilon_{\delta} \neq 0$ . (Note that along the  $\langle 111 \rangle$  direction  $\varepsilon_{\varepsilon} = \varepsilon_{\delta} = 0$ , and  $\Delta(C_{11} - C_{12}) = 0$ .)

The ground twofold degenerate vibronic rotational state  $l_{\varphi} = \pm\frac{1}{2}$  is split by the external strain of above type into two singlet states separated by the energy gap  $b\varepsilon_{\delta}$ . The contribution of these states to the free energy is of the form

$$F = -kT \ln[\exp(-b\varepsilon_{\theta}/2kT) + \exp(b\varepsilon_{\theta}/2kT)] \quad (8)$$

where  $E_0$  is the energy of the ground vibronic state. Then we have

$$\Delta C \equiv \Delta(C_{11} - C_{12}) = -\frac{2}{3}(b^2/kT)[1/\cosh^2(b\varepsilon_{\theta}/2kT)]. \quad (9)$$

Hence if only the ground vibronic state is taken into account, the temperature dependence of the alteration of the elasticity modulus (if no external strain is present;  $\varepsilon = 0$ ) follows the Curie-Weiss relation  $\Delta C \propto 1/kT$ . The excited vibronic states are split by the external strain to a small degree compared with the ground state because of the reduction in the electron-strain interaction. Indeed, the arbitrary perturbation  $V_{\text{tet}}$  (having tetragonal symmetry) of the electronic subsystem of the impurity within the strong-coupling approximation has the form  $V_{\text{tet}} \propto \cos \varphi$ . As can be easily seen, the matrix element of  $V_{\text{tet}}$  calculated with the wavefunctions of the  $n$ th vibronic level differs from zero in the case of the ground rotational state  $l_{\varphi} = \pm\frac{1}{2}$  only. Thus, the splitting of the excited states with  $l_{\varphi} \neq \pm\frac{1}{2}$  occur owing to the small admixture of the state with  $l_{\varphi} \pm 1$  by the external strain and hence the contribution of these states to the change in the elasticity modulus is rather small.

The strain- and temperature-dependent function  $\Delta C(\varepsilon_\delta, T)$  is plotted in figure 2. This function (9) determines the change in the local elastic properties of the crystal near the JT impurity and, in turn,  $\Delta C$  depends on the splitting of the vibronic levels by the external strain and their temperature occupation. As seen from figure 2, for any arbitrary magnitude  $\varepsilon_\delta \neq 0$  the value  $\Delta C \rightarrow 0$  for  $T \rightarrow 0$  or  $T \rightarrow \infty$ . The zero temperatures are equivalent to a large splitting of the degenerate ground state due to the strain, which quenches the change in the elasticity modulus. Indeed, this change becomes zero ( $\Delta C(\varepsilon_\delta) \rightarrow 0$ ) as the strain is increased and  $\Delta C(\varepsilon_\delta = 0) = \Delta C_{\max}$ . For a system with a non-degenerate electronic energy spectrum the change in the elasticity modulus can be shown to have a magnitude  $\Delta C \propto \exp(-\Delta E/kT)$ , where  $\Delta E$  is the gap in the energy spectrum.

### 3. The interacting impurities

In this section the vibrational interimpurity interaction and its influence on the effect of reducing the elasticity modulus of the crystal is discussed. If the concentration of impurities is not high, one can restrict the consideration of the intercentre interactions by coupling each centre with the equivalent nearest neighbour only. (The final result can be averaged over the interimpurity distances.) In the strong-coupling limit under consideration the electrostatic interaction can be shown to result in the redetermination of the effective constant of the interaction via vibrations.

One can write the Hamiltonian of the system in the form

$$H = \sum_{i=1,2} H(i) + H_{\text{int}} \quad (10)$$

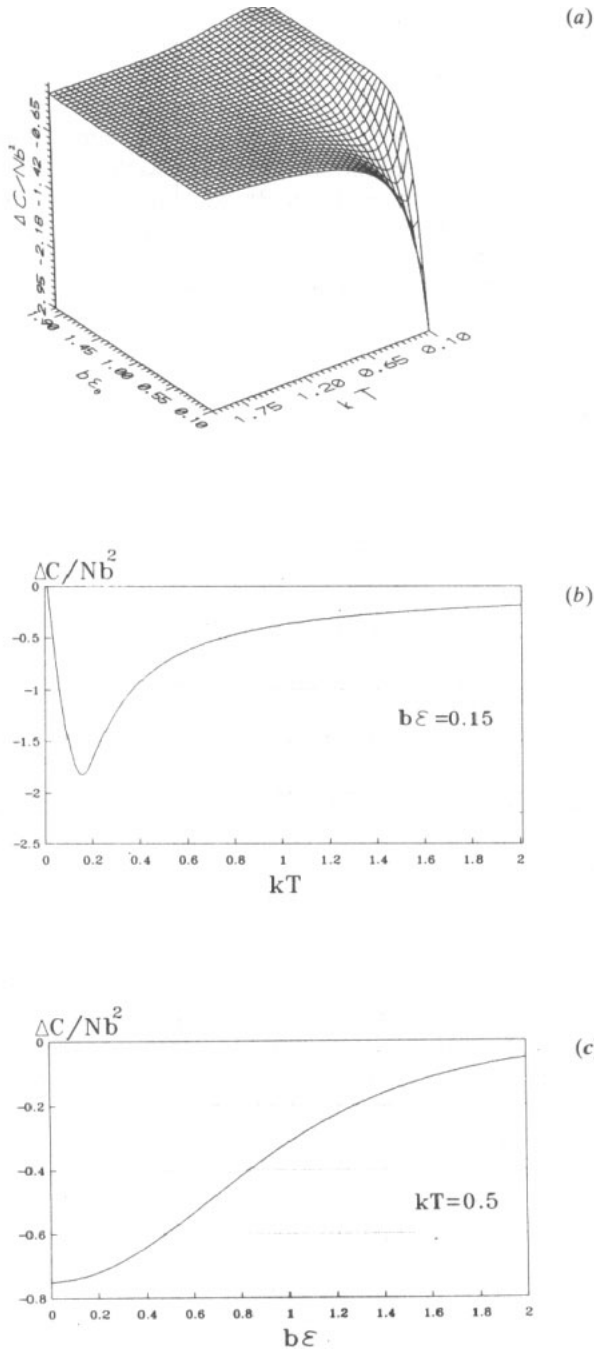
where  $H(i)$  is the Hamiltonian of the single JT centre (1),  $i$  are the coupling centres and  $H_{\text{int}}$  describes the interaction between the centres:

$$H_{\text{int}} = \sum_{\Gamma\gamma\bar{\gamma}} K_{\Gamma\gamma\bar{\gamma}} Q_{\Gamma\gamma}(1) Q_{\Gamma\bar{\gamma}}(2). \quad (11)$$

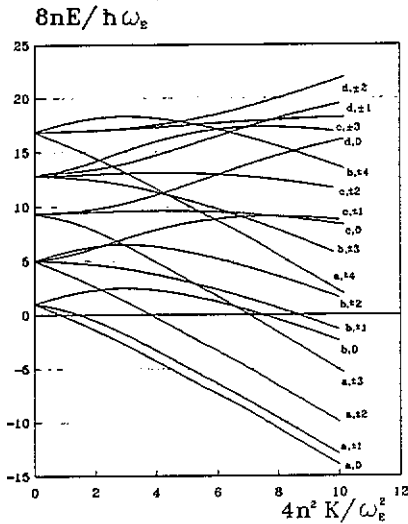
Here  $K_{\Gamma\gamma\bar{\gamma}}$  is the effective constant of the intercentre interaction which mixes the symmetrized local vibrations (the vibrations of the nearest surrounding)  $Q_{\Gamma\gamma}(1)$  and  $Q_{\Gamma\bar{\gamma}}(2)$  of centres 1 and 2, respectively. We restrict our consideration to the case when the ground electronic states of each interacting impurity is twofold orbitally degenerate. It can be shown (Bersuker *et al* 1990) that in the case under consideration with the JT centres in the  $E$  states with strong vibronic coupling with local vibrations of the  $E$  type the maximum contribution to the interaction is caused by the  $E$  vibrations, i.e. the terms in (11) with  $\Gamma = E$ ,  $\gamma$  being equal to  $\bar{\gamma}$ . The contribution of the vibrations of the other symmetry  $\Gamma \neq E$  to the energy of the coupled centres is proportional to  $E_E K_{E\gamma\bar{\gamma}}/\omega_\Gamma^2 \ll E_E$ , since for the distant impurities  $K_{E\gamma\bar{\gamma}}/\omega_\Gamma^2 \ll 1$ . Using the adiabatic electronic basis and diagonalizing the vibronic Hamiltonian  $H_{\text{vib}}$  (2) one can obtain for the lower sheet of the adiabatic potential

$$H = -\frac{\hbar^2}{2} \sum_{i=1,2} \frac{\partial^2}{\partial \rho_i^2} + \frac{\hbar^2}{4\rho_0^2} (L_\xi^2 + L_\chi^2) + \frac{1}{2}\omega_E^2 \sum_{i=1,2} \rho_i^2 - V_E \sum_{i=1,2} \rho_i + K\rho_1\rho_2 \cos(2\xi) - 2b\varepsilon_\delta \cos\chi \cos\xi. \quad (12)$$

Here  $K \equiv K_{E\gamma E\gamma}$ ,  $\xi = (\varphi_1 - \varphi_2)/2$ ,  $\chi = (\varphi_1 + \varphi_2)/2$ . The Hamiltonian (12) is written



**Figure 2.** (a) The change  $\Delta C = \Delta(C_{11} - C_{12})$  in the elasticity modulus versus the temperature and the external strain along (100) in the case of non-interacting impurities.  $N$  is the concentration of the impurity centres. (b) The cross section of the surface  $\Delta c(\varepsilon, T)$  along external strain  $\varepsilon$ . (c) The cross section of the surface  $\Delta c(\varepsilon, T)$  along external temperature  $T$ .



**Figure 3.** Vibronic energy spectrum of two interacting impurity centres versus the constant  $K$  of the intercentre interaction (the eigenvalues of the Hamiltonian (13) with  $b = 0$ ). The total spectrum is formed by two motions that are in-phase and counterphase common reorientations of two centres. Each of the multiplets of levels with labels  $a, b, c, d, \dots$  forms the vibronic spectrum of in-phase common rotation of the two-centre system (along  $\chi$ ) with quantum numbers  $l_\chi = 0, \pm 1, \pm 2, \dots$ . These multiplets are separated by the energy gaps of the hindered counterphase rotation (along  $\xi$ ).  $n = E_{JT}/\hbar\omega_E$ .

for the case when the external strain is along the direction  $\langle 100 \rangle$ . The adiabatic electronic function corresponding to equation (3) is of the form of the product of the two one-centre wavefunctions (4) localized at different sites.

As seen from (12), for the case  $K \ll \omega_E^2$  and  $b\varepsilon_\delta/\hbar \ll \omega_E$  there are two types of motion in the system: motion along the angular degrees of freedom  $\xi$  and  $\chi$  induced by the reorientation of the nuclear configuration, and motion along the radial variables  $\rho_i$ , corresponding to the vibrations near the new equilibrium positions  $\rho_0 \equiv \rho_i^{(0)} = V_E/(\omega_E^2 - K/2)$  at the bottom of the minima with the depth  $E_{JT} = V_E\rho_0$ . These two types of motion induce the two types of interimpurity interaction mentioned in section 1, i.e. angular and radial interactions, respectively. The angular motion describing the collective reorientation of the distortions of  $E$  type around the JT centres and possessing a momentum of inertia given by  $I = 4\rho_0^2$  (12) is slow compared with the vibrations along the  $\rho_i$  degrees of freedom and hence these two types of motion can be separated within the adiabatic approximation (Born and Kun 1954). In this case the energy spectrum of the total system is the superposition of the vibrational (with a gap of the order of  $\hbar\omega$ ) and the angular spectra.

The Hamiltonian of the slow subsystem (near the equilibrium positions  $\rho_0$  of the fast subsystem) is of the form

$$H(\xi, \chi) = (\hbar^2/4\rho_0^2)(L_\xi^2 + L_\chi^2) - K\rho_0^2 \cos(2\xi) - 2b\varepsilon_\delta \cos \chi \cos \xi. \quad (13)$$

In the absence of the external strain ( $b = 0$ ) the variable  $\chi$  is cyclic, i.e. in the space of the variables  $\xi$  and  $\chi$  the surface of the potential energy of the interacting impurities possesses a one-dimensional trough along  $\chi$ . The motion along the trough corresponds to the in-phase reorientation in the same direction as the local  $E$ -type distortions at each impurity centre. Depending on the values of the constant of the intercentre interaction  $K$  the motion along  $\xi$  describing the counterphase rotation of the local distortions can be changed from the free rotation ( $K \rightarrow 0$ ) to the harmonic vibration near the bottom of the appropriate minimum of the potential energy ( $K \propto \omega_E^2$ ). The spectrum of the eigenvalues of the Hamiltonian (13) with  $\varepsilon_\delta = 0$ , which describes the angular interaction between the JT centres, is plotted in figure 3 (Bersuker *et al* 1990). The singlet ground



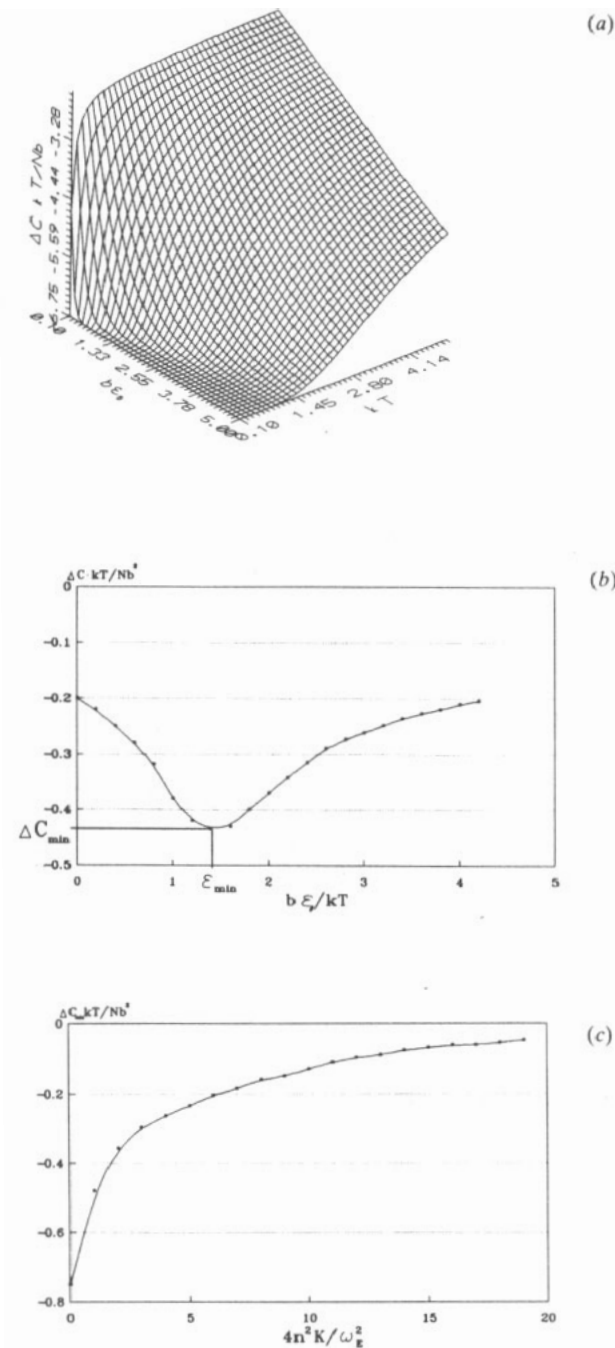
state is the specific feature of the vibronic spectrum of the interacting impurities. This is because the spectrum of the collective rotations along the trough of the adiabatic potential is classified by an integer quantum number of the angular momentum  $l_\chi = 0, \pm 1, \pm 2, \dots$  (unlike the single-centre case) so that the singlet level with  $l_\chi = 0$  corresponds to the ground state.

From (13), the electron-strain interaction deforms the trough and mixes rotational states with quantum numbers  $l_\chi$  which differ by unity. However, with the exception of some particular points (intersection points), such states (see figure 3) are always separated by large energy gaps of the rotational spectrum which results in comparatively small mixing. The strain-dependent function  $\Delta C(\varepsilon_\delta, T)$  in figure 4 was obtained numerically as a result of the diagonalization of the matrix of the electron-strain interaction (13) in the basis of the lowest vibronic states of the system, represented in figure 3. The intercentre interaction is seen to affect considerably the magnitude of the effect of softening and its dependence on strain. First of all the value of the initial softening  $\Delta C(\varepsilon_\delta = 0)$  that essentially results from the non-degenerate ground state of the two-centre system is reduced. The strain-dependent function  $\Delta C(\varepsilon_\delta)$  possesses a minimum the position of which moves (and its depth decreases) as the constant  $K$  of the intercentre interaction is increased. On the whole the effect of the intercentre interaction is that it reduces the softening of the crystal.

#### 4. Discussion

As follows from the arguments given above, the ground state of the system of interacting impurity centres is a singlet that corresponds to the freezing of the motion along the trough of the adiabatic potential in both JT centres. Therefore the interimpurity interaction results in a more rigid lattice compared with a crystal with the same non-interacting centres (in degenerate electronic states).

The magnitude of this effect is convenient to estimate via the ratio of the energy  $E_{\text{int}}$  of the intercentre interaction to the JT energy  $E_{\text{JT}}$  of the single centre (where  $E_{\text{int}}$  is the change in the ground-state energy of two JT centres due to the elastic coupling between them):  $E_{\text{int}}/E_{\text{JT}} = K/(\omega_E^2 - K/2)$ . Taking into account that  $\omega_E^2 = \sum a_\kappa(E\gamma)^2 \omega_\kappa^2$ , where  $a_\kappa(E\gamma)$  is Van Vleck's (1939) coefficient that transforms after the representation  $\Gamma = E$  ( $\gamma$  are its rows) of the point group symmetry of the impurity centre. The sum is taken over all the values of the wavevector and the branches of the crystalline normal vibrations,  $\omega_\kappa$  being their frequencies. An equivalent expression can be written for the constant  $K$  of the interaction between the impurities sited at points 1 and 2:  $K = \omega_{12}^2 = \sum a_\kappa(1E\gamma)a_\kappa^*(2E\gamma)\omega_\kappa^2$ , where Van Vleck's coefficients are localized to sites 1 and 2. Using the explicit form of these coefficients  $a(n\Gamma\gamma) = 0_{\Gamma\gamma, \kappa} \exp(i_\kappa R_n)$ , where  $0_{\Gamma\gamma, \kappa}$  is a matrix element of the orthogonal transformation diagonalizing the dynamical matrix of the crystal,  $R_n$  the position of the  $n$ -site (for the form of  $a_\kappa(n\Gamma\gamma)$ , for some particular cases see Stevens (1969) and Steggle (1977)), and integrating with respect to  $\kappa$ , one can obtain within the Debye approximation  $K/\omega_E^2 = 5x^{-5}[\cos x (6x^{-2} - 1) + 3 \sin x (1 - 2x^{-2})x^{-1}]$ ,  $x \equiv k_D R_{12}$  with  $k_D$  is the value of the Debye wavevector and  $R_{12}$  is the interimpurity separation. In the case of the GaAs crystal with a given value of  $k_D$  and the lattice constant  $a_0$ , one can estimate the interaction energy as follows:  $E_{\text{int}} \approx 0.03E_{\text{JT}}$  provided that the impurities are at the distance of two lattice constants from each other (impurity concentration about 10%). For the GaAs: Cu system with relatively weak JT coupling the value of the JT distortion is assumed to be  $\rho_0 = 0.1 \text{ \AA}$  and, taking



**Figure 4.** (a) The change  $\Delta C \equiv \Delta(C_{11} - C_{12})$  in the elasticity modulus versus the temperature and the external strain along (100) in the case of the interacting impurities.  $N$  is the concentration of the impurity centres. (b) A cross section of the surface  $\Delta C(\epsilon, T)$  along the line  $T = \text{constant}$  (with the arbitrary value of  $K$ ). (c) The dependence of the minimum value of  $\Delta C_{\min}$  on the magnitude of the constant  $K$  of the intercentre interaction.

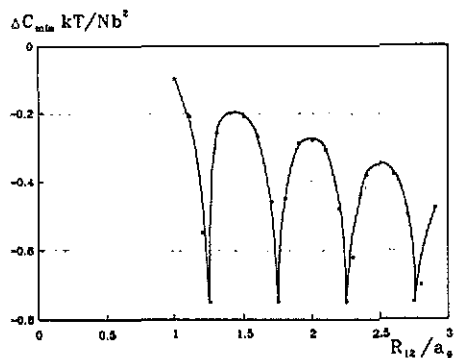


Figure 5. A plot of  $\Delta C$  as a function of the intercentre distance (as an example the case  $E_{JT}/\hbar\omega_E = 5$  is used).

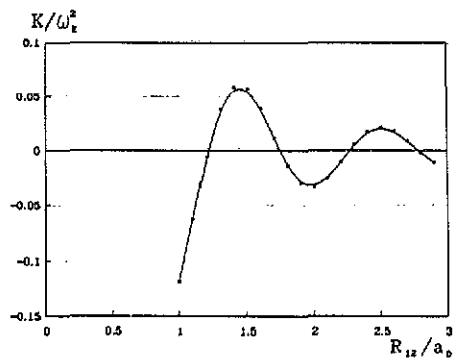


Figure 6. The dependence of the constant  $K$  of the intercentre interaction on the distance between the impurity centres.  $a_0$  is the lattice constant.

the electron-strain constant  $b = 3.15$  eV (Averkiev *et al* 1986), we have  $E_{int} \approx 8$  cm<sup>-1</sup>. In the case of a crystal with a Debye temperature  $T_D$  of about 300 K for impurities with strong JT coupling ( $E_{JT} \approx 2 \times 10^3$  cm<sup>-1</sup>), the energy of the intercentre interaction is of the order of 60 cm<sup>-1</sup>.

The results of the calculations of  $\Delta C(R_{12})$  are plotted in figure 5. The oscillations of  $\Delta C(R_{12})$  are due to the alternation of the sign of the elastic interaction between the impurities as a function of the intercentre distances  $R_{12}$ . Note that the elements of the dynamical matrix  $\omega_{nm}^2$  of the crystal binding different sites  $n$  and  $m$  of the lattice can be both positive and negative (figure 6). We obtain the following estimation:  $\Delta C(R_{12} = 2a_0)/\Delta C(K = 0) \approx 0.12$ , i.e. the change in the elasticity modulus due to the intercentre interaction is about 12% of the magnitude of the effect of softening of the crystal induced by impurities in the twofold degenerate electronic states.

## References

- Averkiev N S, Ashirov T K, Gutkin A A, Osipov E B and Sedov V E 1986 *Fiz. Tverd. Tela* **28** 2959  
 Bersuker I B and Polinger V Z 1989 *Vibronic Interactions in Molecules and Crystals* (Berlin: Springer)  
 Bersuker G I, Polinger V Z, Chibotaru L F and Solonenko A O 1990 *Mol. Phys.* at press  
 Born M and Kun H 1954 *Dynamical Theory of Crystal Lattices* (Oxford: Clarendon)  
 Englman R 1972 *The Jahn-Teller Effect in Molecules and Crystals* (New York: Wiley)  
 Gehring G A and Gehring K A 1975 *Rep. Prog. Phys.* **38** 1  
 Leibfried G 1955 *Gittertheorie der Mechanischen und Thermischen Eigenschaften der Kristalle* (Berlin: Springer)  
 Steggle P 1977 *J. Phys. C: Solid State Phys.* **10** 2817  
 Stevens K W H 1969 *J. Phys. C: Solid State Phys.* **2** 1934  
 Van Vleck J H 1939 *J. Chem. Phys.* **7** 61