Phase transitions in systems with reorienting impurity centres

Phase transitions in systems with reorienting impurity centres

G I Bersuker

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

Abstract. Phase transitions induced by the quenching of reorientations in a system of impurity centres with adiabatic potentials having several equivalent minima are discussed. In addition to inter-centre coupling the transition temperature depends on the interaction between the impurity and the crystal. The interaction of the impurity electronic states with the crystalline vibrations causing the formation of the minima of the adiabatic potential also modifies the density of the crystal vibrations. The latter depends on the impurity reorientation which causes the essential change of the total energy of the crystalline vibrations in the phase transition. The system of Li^+–$KTaO_3$ and Jahn–Teller centres in twofold-degenerate electronic states are considered. The possibility of the formation of a Jahn–Teller glass phase is also discussed.

1. Introduction

Among impurity systems a large class of centres having adiabatic potentials with two or several equivalent minima and hence with several possible equivalent nuclear configurations exists. The most well known examples of such centres are the off-centres impurities in crystals (Narayanamurti and Pohl 1970, Deygen and Glinchuk 1974) and the orbitally degenerate Jahn–Teller centres (Bersuker 1984). In both cases the origin of the two, or several, minima in the adiabatic potential is the same: the vibronic mixing of the electronic states localised at the impurity (either degenerate or ground and excited states) by the lattice vibrations of appropriate symmetry. The system can reorient between these minimal configurations by means of either the off-centre ion jumping between the minima or reorientation of the appropriate near-neighbour deformations (in the case of Jahn–Teller centres).

If the concentration of the impurities is large enough and their interaction is essential, a transition to a new phase in which the local dynamics of the impurities is quenched may take place. Therefore there are two possibilities: (i) all the off-centre ions are displaced (all the round-centre deformations are oriented) coherently resulting in an ordered phase, or (ii) a glass-like phase with disordered centre orientations (similar to the case of spin glasses (Edwards and Anderson 1975)) occurs. The parameters of the phase transition, in particular its temperature, are determined by the balance of the energy changes (during the transition to the new phase) of the impurities and the crystalline matrix, respectively.

One can expect that the injection of the impurity, inducing the multi-well adiabatic potential, results in a considerable redetermination of the spectrum of the crystalline vibrations of appropriate symmetry and hence in the dependence of the appropriate internal energy on the motion of the impurity. Thus the description of the phase transition on the systems under consideration should be based on a detailed consideration of the interaction of the impurity with the lattice.

2. The phase transition temperature

The Hamiltonian H of the impurity–phonon system under consideration includes the Hamiltonians of the impurity centres, H_d, the lattice, H_{lat}, and the interaction between these two subsystems H_{int}, the latter *not* being assumed to be small: $H = H_d + H_{lat} + H_{int}$. It is convenient to divide the total Hamiltonian H into three parts which correspond to the reorientation motion of the impurity H_i, to the crystalline vibrations H_c, modified by the coupling with the impurity, and to the small interaction V_{int} between both parts mentioned above: $H = H_i + H_c + V_{int}$. Considering the reorientation motion as slow in comparison with the lattice vibrations, it is possible to separate these subsystems adiabatically. The smallness of the interaction V_{int} justifies this approximation, its validity being tested in every particular case discussed below. In this case the total free energy of the impurity crystal $F = U + TS$, where U is the internal energy, T the temperature and S the entropy, can be taken as a sum of two main contributions of the crystalline matrix F_c and the impurity subsystem F_i: $F = F_c + xF_i$, where x is the impurity concentration. Here F_c represents the free energy of the crystal in the vibrational spectrum in which the interaction of the electronic states of the impurity with the nuclear vibrations is taken into account. Similarly, F_i corresponds to the single impurity centre, its levels being formed by the same interaction with the crystal. In the form of F used above, it is also assumed that the interaction between the impurities is small. Due to this fact it is possible to write the free energy of the system of impurities as a sum of the terms corresponding to each single centre. The injection of the impurity can be expected to leave the electronic spectrum of the crystal essentially unchanged.

Limiting ourselves to consideration of first-order phase transitions only, it is possible to take the free energy of the 'para-phase' F_p at the critical temperature $T = T_c$ to be equal to that of the 'freezing' phase F_f, $F_p(T_c) = F_f(T_c)$. In this case we obtain

$$T_c = (\Delta U_c + x\Delta U_i)/(\Delta S_c + x\Delta S_i) \tag{1}$$

where $\Delta U_c = U_c^f - U_c^p$ is the difference between the internal energies of the crystal in the corresponding phases, and ΔS_c, ΔU_i and ΔS_i are defined in a similar way. The internal energy of the lattice vibration and the lattice entropy in the 'para-phase' (freezing phase) can be written in the form

$$U_c^{p(f)} = \int \varepsilon(\omega)Z_{p(f)}(\omega)\,d\omega$$

$$S_c^{p(f)} = \int S(\omega, T)Z_{p(f)}(\omega)\,d\omega. \tag{2}$$

In (2) $\varepsilon(\omega)$ is the energy of the harmonic oscillator, $S(\omega, T)$ is its entropy and $Z_{p(f)}(\omega)$ is the density of vibrational states of the crystal in the para-phase (freezing phase). Within the approximation of non-interacting impurity centres the total density of vibrations is

$Z(\omega) = Z_0(\omega) + x\tilde{Z}(\omega)$, where $\tilde{Z}(\omega)$ is the density of those vibrations which can interact with the electronic states of the impurity according to symmetry rules. Neglecting the changes in the elastic characteristics of the crystal at the phase transition, we obtain

$$\Delta U_c = x \int \varepsilon(\omega)\Delta\tilde{Z}(\omega) \, \mathrm{d}\omega$$

$$\Delta S_c = x \int S(\omega)\Delta\tilde{Z}(\omega) \, \mathrm{d}\omega \tag{3}$$

where $\Delta\tilde{Z}(\omega) = \tilde{Z}_f(\omega) - \tilde{Z}_p(\omega)$.

For the impurity centre, the change of the energy ΔU_i can be taken as the difference of the energies ε_f and ε_p of the states occupied before and after the transition: $\Delta U_i = \varepsilon_f - \varepsilon_p = -V(x)$. Here $V(x)$ is the concentration-dependent energy, which responds to the interaction between the impurity centres. As a result expression (1) takes the following form:

$$T_c = \left(V(x) - \int \varepsilon(\omega)\Delta\tilde{Z}(\omega) \, \mathrm{d}\omega\right) \Big/ \left(-\Delta S_i - \int S(\omega, T_c)\Delta\tilde{Z}(\omega) \, \mathrm{d}\omega\right). \tag{4}$$

As it can be seen from (4), the temperature of the phase transition is determined by the effect of the impurity electronic states on the crystalline vibration $\Delta\tilde{Z}(\omega)$. In particular, if at concentrations less than some limiting value x_0 the phase transition in the system is not observable, $T_c \leqslant 0$, then it follows from (1) that $V(x) \leqslant \Delta U_c/x$. In other words, the change in the energy of the impurity subsystem due to the transition to the new phase is compensated by the corresponding change in the energies of lattice vibration. T_c grows with the strengthening of the interaction $V(x)$ as the concentration x increases.

Thus, for further calculation of T_c it is necessary to evaluate the new density of crystalline vibrations $\tilde{Z}(\omega)$, redetermined by the injection of the impurity and hence dependent on its dynamics.

3. Off-centre impurities

Let us consider the activation mechanism of reorientations of the impurities for which $w = w_0 \exp(-E/kT)$, where w is the probability of reorientation and E the activation energy. The system Li^+–$KTaO_3$, which was investigated in some detail (Vugmeister and Glinchuk 1985) can be used as an example of this case. The Li^+ ion, substituted for the K^+ one, is displaced from the lattice point along the direction [100] and jumps between the six equivalent off-centre positions. At a given concentration x of the Li impurities, the system undergoes a transition at $T = T_c$ to the new phase characterised by the 'freezing' of the ion's jumping. When the concentration x changes within the range $1\% \leqslant x \leqslant 9\%$, the transition temperature varies from $T_c = 0$ K to $T_c = 100$ K. The Hamiltonian of the system and the appropriate impurity dynamics were discussed by Bersuker (1988). According to the above discussion, the slow subsystem corresponding to the jumping motion of the ion between the off-centre positions was separated from the fast one which describes the vibrations of the atoms of the crystal, the interaction between these subsystems being small. It was shown that the off-centre displacement of the ion is due to the mixing of the impurity ground electronic states with the excited threefold-degenerate one by threefold degenerate lattice vibrations of the type t_{1u}, which together with the twofold-degenerate ones form the adiabatic potential of the system.

The latter has six minima along the appropriate crystallographic directions. In its turn, the displacement of the Li atom results in a radical redetermination of the t_{1u}-type lattice vibrations, its Green functions having the following form:

$$G_{t_{1u}}(\omega) = [(\overline{\omega^{-2}})^2/2\pi]\{[g_0(\omega) + \overline{\omega^{-2}}]\sin^2\varphi + \overline{\omega^{-2}}g_0(\omega)\omega^2\cos^2\varphi\}$$

$$\times\{[\overline{\omega^{-2}} + g_0(\omega)]^{-1} - [\omega^2\overline{\omega^{-2}}g_0(\omega)]^{-1}\} \tag{5}$$

where $g_0(\omega)$ is the Green function of the initial t_{1u} crystalline vibration (without the vibronic coupling with the impurity), $\overline{\omega^{-2}} = \text{Re }g_0(\omega)|_{\omega=0}$, φ being the angular variable of the t_{1u} nuclear displacements in spherical coordinates. The values $\varphi = 0, \frac{1}{2}\pi, \pi$ and $\frac{3}{2}\pi$ correspond to the four minima of the adiabatic potential (the second spherical coordinate is absent in (5) because of the special choice of the coordinate system). Thus, the reorientation of the impurity between the minima results in an appropriate change in the density of the t_{1u} crystalline vibrations.

The change in the internal energy of the crystal can be estimated using the dependence of the activation energy on the impurity concentration induced by the interaction between the impurities. Following previous estimations (Bersuker 1988) of the experimental data on thermal averaging of the quadrupole structure of the NMR spectra (Van der Klink *et al* 1983), the interaction $V(x)$ changes in the range $750 \leq V(x) \leq 1100$ K as x varies from 1% to 9%. The change in the entropy of the impurity centre can be taken as follows (Eberhart *et al* 1986): $\Delta S_i = \ln(W_f/W_p)$, where W_f and W_p are the numbers of states of the centre in the two phases, respectively. Taking into account that in the 'para-phase' the system is delocalised over all the six minima (in contrast to the single minimum state in the freezing phase) we get: $\Delta S_i \simeq \ln 6$. Neglecting ΔS_c as being small compared with ΔS_i (the validity of this statement is tested below) and substituting in (4) the magnitudes $V(x_0)$ and $T_c(x_0)$ at some value $x = x_0$, one finds: $\Delta U_c/x = 0.19\hbar\omega_0 \simeq 140$ K where $\hbar\omega_0$ is the maximum energy of the appropriate crystalline phonons. Using this value for ΔU_c and the estimations of $V(x)$ given in Bersuker (1988), one obtains good agreement between the calculated T_c via (4) and the experimental values of the phase transition temperatures over the whole range of concentrations x.

Now let us calculate ΔU_c and ΔS_c in an explicit form by the use of (5). In the freezing phase, the system is localised in one of the minima ($\varphi = 0$), and in the para-phase it can be considered approximately as delocalised over all the minima, i.e. $G_{t_{1u}}(\omega)$ from (5) can be averaged over the angle φ. In order to calculate the changes in the internal energy and the entropy (3) it is necessary to set the initial density of the crystalline vibrations $\text{Im }g_0(\omega)$. For the sake of simplicity, the latter can be presented by the model density $\text{Im }g_0(\omega) = A_0\omega^2(\omega_0 - \omega)$ with a maximum frequency $\omega_{max} = \omega_0$. As a result (4) takes the form

$$kT_c[-\Delta S_i - D_0(kT_c/\hbar\omega_0) + D_1(kT_c/\hbar\omega_0)^2] = V(x) - 0.1\hbar\omega_0 \tag{6}$$

where $D_k \equiv \int_0^\infty \Omega^k \ln(1 - e^{-\Omega})\,d\Omega$ and the higher order terms in $kT_c/\hbar\omega_0 \simeq (10^{-1}\text{–}10^{-2})$ are omitted. As can easily be seen, ΔS_c (the second and the third terms in the brackets) are very much smaller than ΔS_i, and the change in the internal energy $\Delta U_c/x = 0.1\hbar\omega_0$ is by its order of magnitude close to the value $0.19\hbar\omega_0$ obtained above, which gives good agreement with the experimental data for T_c. The remaining differences are due to the fact that the calculations were made in a rough approximation using the model density of vibrations $\text{Im }g_0(\omega)$ and the simplified redetermined density $\bar{Z}(\omega) = \text{Im }G_{t_{1u}}(\omega)$ (5) (in particular it was supposed that $\text{Re }g_0(\omega) \gg \text{Im }g_0(\omega)$). To obtain more accurate

estimations, the real density of the crystalline vibrations taking into account its dependence on the concentration of the impurities has to be employed.

4. Jahn–Teller centres

As an example of systems reoriented by tunnelling, we consider Jahn–Teller impurity centres in twofold orbitally degenerate electronic states of type E strongly coupled with the crystalline vibrations of appropriate symmetry. Within the approximation of strong-linear and weak-quadratic vibronic interactions the adiabatic potential of such a system consists of three multidimensional minima in the space of the twofold degenerate symmetrised crystalline vibrations Q_θ and Q_ε of type E, where θ and ε are the rows of the E-representation (Bersuker 1984). The tunnelling of the system between these minima is accompanied by the motion of the wave of lattice deformations around the impurity. As a result of several transformations the total vibrational Hamiltonian of the system (the fast subsystem) takes the form (Bersuker and Polinger 1981)

$$H_c = H(Q_\theta) + \tilde{H}(Q_\varepsilon) + WQ_{1\theta}^2 \cos(3\varphi). \tag{7}$$

Here $Q_{1\theta}$ is the θ-type displacement of the coordination sphere, nearest to the impurity, W the constant of the quadratic vibronic coupling (the small parameter), φ the angular variable of the nuclear displacements (the values $\varphi = 0$, $\tfrac{2}{3}\pi$, $\tfrac{4}{3}\pi$ corresponding to the minima of the adiabatic potential), $H(Q_\theta)$ the Hamiltonian of the initial θ-type harmonic vibrations, $\tilde{H}(Q_\varepsilon)$ is the Hamiltonian of ε-vibrations, radically redetermined by the vibronic interaction (in a manner similar to (3)). The density of vibrations corresponding to the Hamiltonian $\tilde{H}(Q_\varepsilon)$ as seen from (7) does not contain the variable φ and hence it does not change with the transition to the 'freezing' phase, $\Delta\tilde{Z}_\varepsilon = 0$. On the other hand, the effect of the vibronic interaction on the θ-vibrations is reduced to a weak local perturbation, described by the term $WQ_{1\theta}^2 \cos(3\varphi)$ in (7), which can result in a pseudo-local vibration (similar to the case of the isotopic defect in the lattice dynamics). This means that the initial density of θ-vibrations remained practically invariant during the reorientation, $\Delta\tilde{Z}_\theta = 0$. It should be noted that the weak dependence of the density of the redetermined crystalline vibrations on the motion of the impurity subsystem is due to the weak quadratic vibronic coupling resulting in the low barriers between the minima of the adiabatic potential. (In the case of linear vibronic coupling, $W = 0$, the adiabatic potential surface possesses an equipotential continuum of minima along the φ axis, there is an integral of motion $\partial/\partial\varphi$ in the system, and the reorientation motion of the impurity centre separates exactly from the lattice vibrations). Thus we obtain from (4)

$$kT_c = V(x)/\Delta S_i \simeq 0.9V(x). \tag{8}$$

To estimate the value ΔS_i we insert in (8) $\Delta S_i \simeq \ln l = \ln 3$, where l is the number of minima of the adiabatic potential. Thus, in a system of Jahn–Teller centres, transition to the phase in which each centre is located in one of its distorted configurations is possible as a result of their interaction. The question of interest concerns the character of the phase generated in this way, in particular the possibility of formation of Jahn–Teller glass (Mehran and Stevens 1983). The displacement of the atoms of the nth coordination sphere of the Jahn–Teller centre due to the coupling of the electrons of the

centre with the crystalline vibrations in the case under consideration is as follows (Bersuker and Polinger 1981):

$$Q_n = V\omega_{n1}^{-2}/[1 - 2W\omega_{11}^{-2}\cos(3\varphi)]. \tag{9}$$

In (9), V is the constant of the linear vibronic coupling, $\omega_{n1}^{-2} = \Sigma_\kappa a_\kappa(n)a_\kappa(1)\omega_\kappa^{-2}$, where the summation is taken over all the wavevectors and the branches of the crystalline vibrations, $a_\kappa(n)$ being the Van Vleck coefficients of the n-th coordination sphere and ω_κ are the frequencies of the normal vibrations. If, for the sake of simplicity, one neglects the dependence of the polarisation unit vectors $e(\kappa)$ on the value of κ (the scalar model of the crystalline vibrations), then the dependence of the distortion $Q_n(r)$ of the lattice on the distance r to the centre $r = (r_n - r_1)$ (where r_n and r_1 are the radius vectors of the n-th and first coordination sphere, respectively) is determined by the expression

$$Q_n(r) \simeq \sum_\kappa{}' e^{i\kappa r}\omega_\kappa^{-2} \sim \frac{1}{r}\left(\kappa_0 r - \frac{(\kappa_0 r)^3}{3 \times 3!} + \frac{(\kappa_0 r)^5}{5 \times 5!} - \cdots\right). \tag{10}$$

Here κ_0 is the maximum value of the wavevector and the dispersion minimum for the acoustic vibrations $\omega_\kappa = c\kappa$ is employed. In the right-hand expression in (10) the first terms of the series for the integral sinus are given. As can easily be seen, the $Q_n(r)$ changes sign when the distance r to the impurity centre reaches the value determined by the inequality $\kappa_0 r' \geqslant 4.2$. At $r = r''$, $\kappa_0 r'' \sim 5.8$, $Q_n(r)$ changes sign again, and so on. Thus the space around the impurity centre is divided into domains, each of which can include several coordination spheres, the distortions of the lattice in them induced by the vibronic interaction having alternating signs. Since the interaction alternating in sign can be assumed to be the main driving force to the glass-like phase, one can conclude that the system of Jahn–Teller centres with strong enough vibronic coupling undergoes a transition to a Jahn–Teller glass at $T = T_c$ (8).

5. Discussion

As follows from (4), the dependence of the temperature T_c of the phase transition on the impurity concentration is determined by the interaction between the impurity centres, while the magnitude of T_c is also chiefly affected by the number l of the minima of the adiabatic potential ($\Delta S_i \simeq \ln l$) and by the nature of the impurity–lattice coupling $\Delta\tilde{Z}(\omega)$. The relatively low phase transition temperatures in the Li^+:$KTaO_3$ system, where there is a rather strong interaction between the impurities, are due to the considerable redetermination of the density of vibrational states, which depends on the impurity reorientation, and hence to the essential changes in the internal energy of the lattice vibrations in the phase transition.

Considering the expressions (4) and (8) one can make some conclusions concerning the effect of the impurity on the vibrations of the crystal. If the phase transition temperature of the system of impurities is essentially different from the value of the inter-impurity interaction, then a considerable redetermination of the density of the appropriate lattice vibrations due to coupling with the impurity electrons can be expected. On the other hand, the relatively high temperatures $T_c(x)$ for the $Pb_{1-x}Ge_xTe$ system (Takaoka and Murase 1979) allows one to assume that $V(x) - \Delta U_c$ is sufficiently large. In the case of Li^+–KCl the Green function is similar to $G_{t_{1u}}(\omega)$ (5) (Bersuker and Polinger 1984), but the interaction between the impurities can be expected to be essentially weaker. Hence one can conclude that the transition to the freezing phase is possible

only for a sufficiently high concentration of the impurities $\tilde{x}$, when the numerator in (4) becomes positive. Assuming, in a manner similar to the case of $KTaO_3$, that $\Delta U_c/x \simeq (0.1-0.2)\hbar\omega_0$, where ω_0 is the maximum frequency of the crystalline vibrations in KCl, one obtains the estimation of the magnitude of the interimpurity interaction $V(\tilde{x}) \simeq (0.1-0.2)\hbar\omega_0$. The temperatures of the transitions to the new phase at $x > \tilde{x}$ have to be somewhat lower than in the case of $KTaO_3$, since in the case of Li^+-KCl the number of minima is $l = 8$. On the contrary, the transition to the phase of Jahn–Teller glass for centres in the twofold-degenerate electronic state can, according to (8), be expected to occur at low concentrations.

Acknowledgments

References

Bersuker G I 1988 *Phys. Status Solidi* b **148** 243
Bersuker G I and Polinger V Z 1981 *Sov. Phys.–JETP* **53** 930
—— 1984 *Phys. Status Solidi* b **125** 401
Bersuker I B 1984 *The Jahn–Teller Effect and Vibronic Interactions in Modern Chemistry* (New York: Plenum)
Deygen M F and Glinchuk M D 1974 *Sov. Phys.–Usp.* **114** 296
Eberhart M E, Johnson K H, Adler D and O'Handley R C 1986 *J. Non-Cryst. Solids* **83** 12
Edwards S F and Anderson P W 1975 *J. Phys. F: Met. Phys.* **5** 965
Mehran F and Stevens K W H 1983 *Phys. Rev.* B **27** 2899
Narayanamurti V and Pohl R O 1970 *Rev. Mod. Phys.* **42** 201
Takaoka S and Murase K 1979 *Phys. Rev.* B **20** 2823
Van der Klink J J, Rytz D, Borsa F and Hochli U T 1983 *Phys. Rev.* B **27** 89
Vugmeister B R and Glinchuk M D 1985 *Sov. Phys.–Usp.* **146** 459