*Materials Science-Poland, Vol. 23, No. 3, 2005*

# Molecular impurity ions as centres with charge transfer degrees of freedom. Influence on ferroelectric phase transitions

V.S. VIKHNIN[1], T.I. MAKSIMOVA[1], J. HANUZA[2, 3*]

[1]AF Ioffe Physical-Technical Institute Russian Academy of Sciences, 194021, St.- Petersburg, Russia

[2]Institute for Low Temperature and Structure Research Polish Academy of Sciences, Wroclaw, Poland

[3]Department of Bioorganic Chemistry, Faculty of Engineering and Economics, University of Economics, Wrocław, Poland

The concept of molecular impurity ions (MI) as centres with charge transfer degrees of freedom, interacting (through the order parameter of the phase transition) with local vibrations and non-soft phonons, as well as with light, has been developed. It has been shown that MI can significantly influence a ferroelectric phase transition (FPT) due to a direct interaction of their specific charge transfer degrees of freedom with the ferroelectric order parameter. In this work, we predict a significant increase of the FPT critical temperature when increasing the MI concentration. The $MnO_4^-$ molecular impurity ions embedded in ferroelectric crystals (e.g. molybdates, tungstates, chromates, phosphates) are considered as possible candidates capable of inducing this effect.

Key words: *molecular impurity ions; charge transfer; ferroelectric phase transition; critical temperature*

## 1. Introduction

The influence of defects on FPT is one of key topics (see, e.g., [1]) research into modern ferroelectric materials. Its possible role in solving the problem of real ferroelectrics is one of the major reasons for this interest. This is important from the point of view of basic sciences as well as applications. In this context, MI doped into ferroelectrics, for example $MnO_4^-$ (as impurity ions) in ferroelectric phosphate, tungstate, molybdate, and chromate crystals, are responsible for a principally new situation arising in the field of FPTs influenced by impurities. Indeed, MIs provide a new possibility for strengthening the influence of defects on FPT due to their specific properties.

*Corresponding author, e-mail: hanuza@int.pan.wroc.pl

Here we deal with a pronounced covalent contribution to ionic-covalent type bonding within MI with significant charge transfer effects. The latter leads to the appearance of new degrees of freedom, characteristic of MI, which directly interact with the ferroelectric order parameter of the matrix. These are charge transfer degrees of freedom connected with fluctuations of charge transfer magnitude relative to its equilibrium value. It is important to note that these charge transfer degrees of freedom $\{q_i\}$ take part in the bi-linear interaction with fluctuations of the soft matrix TO-polarization. This leads to a new origin of the influence of impurities on FPT phenomena. The purpose of the present work is a theoretical consideration of the influence of MI on FPT, taking into account the MI charge transfer degrees of freedom mentioned above. It will be shown that the pronounced increase of FPT temperature can be induced by MIs in this case.

In our first article [2] devoted to the development of the same idea we considered another limiting case of the strong "charge transfer – local lattice vibration" interaction within MI. Such a situation led to a specific resonance increasing the critical temperature of the FPT. This approach takes into consideration the appearance of the well-localized non-Coulomb charge transfer vibronic excitons (see [3, 4] and references therein) in the MI state spectrum. In the present article, we consider an opposite limit, at which the charge transfer–local lattice vibration interaction within MI mentioned above is weak, in agreement with the assumption of the model. This approach seems to be reasonable and necessary for a complete coverage of the problem. Moreover, strong and weak charge transfer–local lattice vibration interaction states can co-exist in real MI as low-lying and higher lying states. Therefore, in reality we deal with both types of states, simultaneously affecting the MI-induced critical temperature increase. The domination of either type of these states depends completely on quantitative values of the parameters. Here we shall consider a situation where the charge transfer fluctuations are purely electronic ones.

$MnO_4^-$ impurity ions doped into the model ferroelectric crystals will be discussed as an example of impurities with well-defined charge transfer degrees of freedom which can directly interact with the soft lattice of the matrix. $MnO_4^-$ impurity ions can replace $XO_4^-$ complexes (X = P, Mo, W, Cr) in the host lattices and manifest a good covalent bonding within molecular ions accompanied by significant equilibrium charge transfer (see [5–9] and references therein).

The results of calculations performed on the basis of the Self Consistent Field $X_\alpha$-Scattered-Wave method [5, 6] suggest that this is the case for $MnO_4^-$ ions. In this context, we will consider the $M^{I}M'^{I}_2(XO_4)_{1-x}(MnO_4)_x$ crystal (where $x$ is the relative concentration of the $MnO_4^-$ MI). Here we consider the electron-lattice mechanism for the influence of impurities on the ferroelectric phase transition. Note that it is principally different from a pure vibration mechanism, which is much weaker on one hand, and usually leads to a decrease in the critical temperature on the other hand. In our case, the electronic gaps between active initial electronic states are of the order of 1–3 eV, and electron–lattice interaction mixes of these initial electronic states with such gaps. Related lat-

tice variables (soft polarisation $P$) are slow as compared with the above-mentioned electronic degrees of freedom and take direct part in the phase transition phenomenon. A corresponding scenario develops under adiabatic conditions, namely new terms in the free energy, which are proportional here to $P^2$, are responsible for the impurity-induced shift of the critical point for the ferroelectric matrix. A similar approach has been successfully used earlier for considering the influence of Jahn–Teller impurities on the ferroelectric phase transition [10, 11].

In spite of the soft critical behaviour of the order-disorder degrees of freedom in the $XO_4^-$ ions-containing crystals, the structure of their order parameters is more complicated than for pure contributions of the order-disorder type. This is the case for improper ferroelectrics [12], in which a soft mode has an order-disorder origin but the resulting polarization is of a displacive-type. Such a phenomenon can be described by the well known pseudo-spin–lattice interaction model (Kobayashi model, [12]). Namely, such a displacive-type polarization mentioned above takes part in the formation of a linear vibronic interaction with the electronic degrees of freedom of $MnO_4^-$ impurity ions in parallel with linear pseudo-spin mode– $MnO_4^-$ electronic degrees of freedom interaction in the framework of our model. Nevertheless, here we take into account also the direct interaction of soft order-disorder type mode with $MnO_4^-$ ion electronic degrees of freedom. It will be shown that the latter circumstance leads to the addition of a positive shift to the FPT critical temperature $T_c$. Such an effect, related to the order-disorder component of the order parameter of FPT, will only induce an addition increase of $T_c$ with respect to the displacive-type component effect.

The $MnO_4^-$ MI is a very effective optical probe. It is characterized by intense ligand-to-metal charge-transfer absorption bands in the VIS range and well pronounced d–d absorption bands in the red region of the spectrum [7–9, 13]. Also, the multi-phonon resonance Raman spectra and the excitation profiles of Raman scattering of $MnO_4^-$ ions in ionic crystals have been studied thoroughly (see [14] and references therein). Recently, intensive NIR-luminescence has been discovered for $MnO_4^-$ molecular ions embedded in cubic [15, 16] and non-cubic [13, 17] crystal lattices.

Such a set of characteristic properties leads to additional new aspects of the problem under investigation. First, it is related to the possibility of the optical excitation of MI in the ferroelectric matrix. The electronic occupation of excited MI-states can significantly change the properties of MI charge transfer and local distortion of the subsystems. As a result, the MI influence on FPT will be changed by the action of optical pumping. Thus, photo-induced effects in FPT phenomena can be expected. Second, investigations of FPT order parameter behaviour (for instance, its critical temperature dependences) involving optical studies of electronic and vibronic spectra of MI embedded in soft matrices seems fruitful. Let us now consider the effect of MI-induced increase of FPT critical temperature predicted in the present work.

## 2. Increase of critical temperature induced by the interaction of soft polarization with molecular impurity ions

Let us evaluate the shift ($\Delta T_C$) of the FPT point induced by the interaction between MI charge transfer on the one hand and soft lattice polarization on the other. We shall consider the case of a uniaxial ferroelectric crystal doped with MIs. Here we shall treat the combined phase transition in the crystal as a combined displacive and order -disorder type of behaviour. The displacive-type component is very significant in such mixing [18]. Note that the static behaviour of improper ferroelectrics of the $XO_4^-$ ion -containing type (with the same symmetry for order-disorder and displacive-type order parameters) is identical to that of proper ferroelectrics (for instance displacive type ferroelectrics). We shall consider in this section the case of a dominating displacive -type order parameter (soft polarization) for the interaction with $MnO_4^-$ degrees of freedom. In our approach we also use the mean field approximation, whose validity stems from the long-wave ($k \approx 0$) order parameter. As a result, the MI-induced renor-malization of the free energy coefficients for the Landau expansion of the free energy can be considered.

Let us briefly discuss here the arguments for grounding the possibility of inserting $MnO_4^-$ into an $XO_4^-$ ion-containing matrix. First, it is known that $MnO_4^-$ molecular ions exist in the framework of ionic-covalent bonding, with an essential contribution to the covalent part [5–9]. Even in the ionic approach, however, the ionic radii for topical $Mn^{5+}$ and $P^{5+}$, $Mo^{6+}$ or $W^{6+}$ ions in the four-fold oxygen coordination do not differ strongly from each other (0.47 Å and 0.31 Å, respectively). Such a difference (0.16 Å) is of the order of zero point vibration fluctuations on one hand, and on the other can be compensated by the pronounce pliable behaviour of four oxygen ions in the framework of a real ionic-covalent regime with important covalent contribution. Second, in this context the successful experimental activity of Güdel et al. for the growing different crystals with $MnO_4^-$ impurities should be underlined (see [13, 17] and corresponding references therein) as well as recent positive result of Hanuza and co-workers [19] for growing the ferroelastic crystal $K_3Na(CrO_4)^{2-}$:$(MnO_4)^{2-}$ with $MnO_4^-$ molecular impurity ions.

The topical assumptions regarding MI are the following:

- The main assumption relating to the active O- and Mn-ion charge transfer states of $MnO_4^-$–MI is the assumption of their good self-localization in the system of host matrix states. Therefore we assume that we are dealing with local or quasi-local electronic states of the $MnO_4^-$ impurity ion, which is an experimental example under discussion.
- The second assumption relating to the active charge transfer states of MI is the assumption of their coherent nature. These are four oxygen ion charge transfer states considered to be coherent states.

• The $MnO_4^-$ impurity ion displays significant covalent O–Mn bonding as mentioned above. Here, the O–Mn covalent bonding coefficient can be estimated as $\gamma_{Mn\text{-}O} \approx 0.44$ and the corresponding equilibrium O–Mn charge transfer value can be high enough (see references [5, 6]). This leads to a decrease of the oxygen ion local negative charge due to O→Mn charge transfer, and to the occurrence of equilibrium oxygen hole states that are well defined within the $MnO_4^-$ MI.

Taking into account these three statements, we deal with a fully-symmetric coherent ground state for oxygen holes (the singlet *A* state). The excited state here is a triplet *T*-state ($T_x$, $T_y$, $T_z$) for the four oxygen equilibrium holes in the cubic ($T_d$) field of the isolated $MnO_4^-$ molecular impurity ion. These *A*, $T_x$, $T_y$, and $T_z$ charge transfer oxygen hole states differ from each other by their different charge distributions among four oxygen ions in accordance with the state symmetry. Thus, the mixing of these states due to an interaction of soft polarization and the order-disorder pseudo-spin related order parameter with such a quartet of oxygen hole states mentioned above corresponds to charge transfer effects.

• The fourth assumption is related to the possibility of using the *A*, $T_x$, $T_y$ and $T_z$ charge transfer oxygen hole states mentioned above in the framework of real situations for $MnO_4^-$–MI embedded in an $XO_4^-$ ion-containing matrix. We shall assume here for simplicity that the splitting of such a triplet of *T*-states in an uniaxial crystalline field of the matrix is much smaller than the splitting ($\Delta_{CT}$) between *T* and *A* charge transfer states in a cubic $T_d$ field for isolated $MnO_4^-$ molecular impurity ions. As a result, such a uniaxial crystalline field of the host lattice could be inessential within our problem analysis with respect to the strong field of molecular origin. Note that the $\Delta_{CT}$ value can be of the order of 1 eV ($\Delta_{CT}$ = 1 eV in our case). Such a value for $\Delta_{CT}$ is typical of oxygen-related energy splitting, for instance for the width of subbands induced by electronic dispersion within the oxygen-related valence bands in oxides. Therefore let us also assume that $MnO_4^-$ impurity ions keep the point group symmetry $T_d$, which is a good approximation for strong molecular bonding related to the crystalline field effect.

Let us start from a phenomenological consideration of the problem. As regards a pure $XO_4^-$ ion-containing matrix, soft lattice dynamics will be related to the new pseudo-spin soft mode with Cochran-type critical dependence (with the $\eta$ variable) and the low frequency polarization mode (with the $P_z$ variable), but without critical softening at definite temperature. Such a soft polarization mode subsystem couples with interacting pseudo-spins of the matrix as in the case of KDP (the Kobayashi model [12]). As a result, the free energy of the pure system without MI can be presented in the following form:

$$\delta F_0 = \frac{1}{2}\alpha(T - T^{(0)})(\eta_z)^2 + \frac{\omega_p^2}{2}(P_z)^2 + AP_z\eta_z + \frac{\beta}{4}(\eta_z)^4 + \ldots \qquad (1)$$

where $T^{(0)}$, $\omega_p$, $A$, $\beta$ are the critical temperature for soft pseudo-spin mode condensation, the frequency for soft polarization (normalized with respect to the vibration mass coefficient), the coefficient for polarization – pseudo-spin order parameters bi-linear interaction, and the fourth order anharmonicity coefficient of the pseudo-spin order parameter, respectively. Minimization of the free energy equation with respect to $P$, $\eta$ allows one to obtain the FPT temperature ($T_C$) equation, which manifests the increase in $T_C$ induced by bi-linear $P\eta$ interaction:

$$T_C = T^{(0)} + \frac{A^2}{\alpha\omega_p^2} \tag{2}$$

The microscopic origin of the interaction between the MI charge transfer degrees of freedom and the FPT order parameter (soft polarization $P_i$) is the effect of A-T state mixing by such an order parameter. The corresponding interaction Hamiltonian can be presented in the following form:

$$\hat{H}_{\text{CT-polarization}} = V_i \sigma_x^{(i)} P_i \tag{3}$$

Here, $\sigma_x^{(i)}$ is a Pauli matrix, $\sigma_x^{(i)} = |T_i\rangle\langle A| + |A\rangle\langle T_i|$, $V_i$ is the vibronic parameter for the interaction between charge transfer and soft polarization. Taking into account the second order perturbation theory with respect to the Hamiltonian in (3), we obtain the following, related to the harmonic contribution of $P_z$ (soft polarization along the main axis) to the Landau expansion for free energy:

$$\delta F_P = \frac{\omega_p^2}{2}(P_z)^2 - \frac{nV_z^2}{\Delta_{\text{CT}}}(P_z)^2 \tag{4}$$

where $n$ is the concentration of MI ($MnO_4^-$ ions, for example). Equation (4) remains in its old form after replacing $\omega_p^2$ by $\tilde{\omega}_p^2$ given by

$$\tilde{\omega}_p^2 = \omega_p^2 - \frac{2nV_z^2}{\Delta_{CT}} \tag{5}$$

After substituting Eq. (5) into Eq. (2), we finally get

$$T_C = T^{(0)} + \frac{A^2}{\alpha[\omega_p^2 - 2nV_z^2(\Delta_{\text{CT}})^{-1}]} \tag{6}$$

As can be seen in Eq. (6), the increase of the FPT critical temperature ($\Delta T_C > 0$) induced by increasing concentration has a non-linear character and can be defined for appropriately small concentrations by Eq. (7):

$$\Delta T_C = \frac{2nV_z^2}{\Delta_{CT}\omega_p^2}\left(\frac{A^2}{\alpha\omega_p^2}\right) \tag{7}$$

After substituting into Eq. (7) reasonable values for $MnO_4^-$ impurity ion parameters in order to estimate the effect under consideration ($\Delta_{CT} \approx 1$ eV, $V_z \approx 10$ D, $\omega_p^2 \approx 0.036$, $A^2/\alpha\omega_p^2 \approx 10$ K and the concentration $n \approx 3\times10^{20}$ cm$^{-3}$), we obtain the critical temperature shift of $\Delta T_C \approx 10$ K. We conclude that the effect predicted in the present paper is large enough to be detected experimentally.

The theoretical considerations presented above describe the effect of molecular impurity ions on a ferroelectric (or ferroelastic) phase transition in crystals built from tetrahedral $XO_4^-$ ions. The pseudo-spin approach is proposed in order to predict the temperature behaviour of these samples. In order to verify these effects, the syntheses of two crystals have been undertaken: $KH_2PO_4$ and $K_3Na(CrO_4)_2$, both doped with $MnO_4^-$ ions. These two host systems differ substantially from each other. In the KDP crystal, these effects are influenced by hydrogen bonding [20–23]. Other effects could also appear in this crystal, i.e. a considerably different proton affinity of the $MnO_4^-$ and $PO_3^{3-}$ ions. This may lead to nano-regions of reorganized hydrogen bonds. The molecular structure and dielectric properties of the KDP crystal may therefore be changed [23, 24]. Relaxor-type behaviour could influence the phase transition parameters in such cases.

The other host matrix, of the $K_3Na(CrO_4)_2$ type, differs from KDP-like crystals due to smaller differences between the charges of the tetrahedral $CrO_4^{2-}$ ion and doped $MnO_4^-$ ion as well as due to a lack of hydrogen bonds. In spite of the different compositions and structures of these two host systems, we expect that the effect of the impurity ions on their phase transitions will be similar. Our preliminary temperature dependent studies of the shape of the ESR signal in the chromate crystal show that the phase transition temperature agrees well with predictions [19].

**Acknowledgements**

Authors are grateful to Prof. A.A. Kaplyanskii for attention to this work that was supported partly by RFBR (04-02-17633).

## References

[1] STRUKOV B.A., LEVANYUK A.P., *Physical fundamentals of ferroelectric phenomena in crystals* (in Russian), 2nd Ed., Moscow, Nauka, 1995.
[2] VIKHNIN V.S., MAKSIMOVA T.I., Ferroelectrics, 299 (2004), accepted for publication.
[3] VIKHNIN V.S., Solid State Communications, 127 (2003), 283.
[4] VIKHNIN V.S., EGLITIS R.I., KAPPHAN S.E., BORSTEL G., KOTOMIN E.A., Phys. Rev. B 65 (2002), 104304.
[5] JOHNSON K.H., Int. J. Quantum Chem., 5S (1972), 143.
[6] JASINSKI J.P., HOLT S.L., J. Chem. Phys., 63 (1975), 1304.

[7] MARTIN T.P., ONARY S., Phys. Rev. B 15 (1977), 1093.
[8] MAKSIMOVA T.I., MINTAIROV A.M., Phys. Solid State, 29 (1987), 813.
[9] MAKSIMOVA T.I., VOGELSANG, H. STOLZ H., VON DER OSTEN W., Solid State Commun., 92 (1994), 337.
[10] VIKHNIN V.S., Fiz. Tver. Tela, 23 (1981), 2370.
[11] KRISTOFFEL N.N., Fiz. Tver. Tela, 23 (1981), 3267.
[12] BLINC R., ZEKS B., *Soft Modes in Ferroelectrics and Antiferroelectrics*, North-Holland Publ. Comp., Amsterdam, 1974
[13] BRUNOLD T.C., HAZENKAMP M.F., GÜDEL H.U., J. Luminescence, 72–74 (1997), 164.
[14] MAKSIMOVA T., Spectrochim. Acta, Part A, 55 (1999), 1153.
[15] MAKSIMOVA T., HERMANOWICZ K., MACALIK L., HANUZA J., J. Mol. Structure, 563–564 (2001), 353.
[16] MAKSIMOVA T., HANUZA J., HAPPEK U., J. Alloys Comp., 341 (2002), 239.
[17] BRUNOLD T.C., GÜDEL H.U., Inorganic Chemistry, 36 (1997), 1947.
[18] BUSSMANN-HOLDER A., DALAL N., *Fundamental Physics of Ferroelectrics 2001*, Virginia, Williamsburg, 2001, AIP Conf. Proc., H. Krakauer (Ed.), 582, pp. 137–143.
[19] HANUZA J., MACZKA M., HERMANOWICZ K., MAKSIMOVA T., in preparation.
[20] ICHIKAWA M., MOTIDA K., YAMADA N., Phys. Rev. B, 36 (1987), 874.
[21] KATRUSIAK A., Phys. Rev. B, 48 (1993), 2992.
[22] KATRUSIAK A., Phys. Rev. B, 51 (1995), 589.
[23] KATRUSIAK A., SZAFRAŃSKI M., Organic Lett., 5 (2003), 1903.
[24] SZAFRAŃSKI M., KATRUSIAK A., J. Phys. Chem. B, 108 (2004), 15709.

*Received 25 November 2004*
*Revised 10 March 2005*