in the outer regions of the $3d$ shell,[40] therefore overlap integrals (and $\langle\varphi|H|\Delta\rangle$ matrix elements essential to the evaluation of $10Dq$) are relatively severely affected while the repercussions on ζ_m are comparatively slight. Given the expanded (or otherwise modified) basis orbitals, the analysis developed in this paper can be reapplied.[41] Such an effort is beyond the scope of the present paper.

One of the great achievements of the transferred hyperfine investigations[1] was, despite uncertainties, the contact made with covalent mixing. The present effort has attempted to provide similar contact between the g shift and covalency. We leave it to the reader to decide for himself how successful this has been. In our opinion it is as, or almost as, effective as the transferred hyperfine data reduction process. The resulting γ_π has proven to be of the same magnitude as γ_σ contrary to common expectation concerning chemical bonding. Introduction of such factors as $3d$ orbital expansion is not expected to radically alter this tendency, i.e., it will similarly reduce both γ_π and γ_σ.

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[40] See Fig. 4 of R. E. Watson, Phys. Rev. **118**, 1036 (1960) for an indication of how an iron series $3d$ shell varies radially with ionic charge.

[41] When doing this, one should not assume a simple one-electron spin-orbit operator of the form of terms in Eq. (3), when evaluating ζ_m and ζ_L, but should use the full ionic spin-orbit operators including two-electron terms (see Ref. 9).

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Influence of Impurities on the Curie Temperature of Ferroelectric Crystals

V. Dvořák and P. Glogar
Institute of Physics, Czechoslovak Academy of Sciences, Prague, Czechoslovakia

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The method of Green's functions is used to derive an expression for the susceptibility of an ionic crystal with defects in a homogeneous electric field in a harmonic approximation. For the sake of simplicity, the polarizability of the ions is not considered and the general expression is specialized for the case of isovalent substitutional impurities. Using the temperature dependence of an anomalously low frequency $[\omega^2=\gamma(T-T_C)]$ of one transverse optic mode of vibration of long wavelength in ferroelectric crystals, it is shown that the influence of such defects on the static dielectric constant is seen as the shift of the Curie temperature, as is known experimentally. The Curie-temperature shift is expressed by means of the force constants between ions, and in the crystal model in question it depends linearly on the concentration of impurities in a broad range of concentrations. The Curie-temperature shift is used to estimate the magnitude of the relative change in frequency of the anomalous optic ("ferroelectric") mode in the (Ba,Sr)TiO$_3$ crystal, which could be determined by the inelastic scattering of neutrons.

I. INTRODUCTION

RECENTLY Vinogradov[1] (see also Ref. 2) dealt with the theory of dielectric losses at microwave frequencies in ionic crystals with a nonideal lattice and, for example, for SrTiO$_3$, he qualitatively explained the frequency dependence of the losses.[3] In the present paper we shall deal with the opposite case, i.e., the influence of defects on the real part of the dielectric constant at low frequencies far enough from resonance. This problem is particularly interesting in ferroelectric substances in which, as is described comprehensively in Ref. 4, crystal lattice defects (particularly different mixtures of impurity ions) greatly influence the static dielectric constant. This influence can usually be expressed by a change only in the Curie temperature T_C while the character of the temperature dependence of the dielectric constant remains practically unchanged. For this reason, it is enough for our purposes to start, out from the Hamiltonian similar to the one in Ref. 1, in which the potential energy contains terms up to the second power in the components of the ionic displacements from their equilibrium positions in the defect lattice.

Various impurities influence the Curie temperature T_C of the same material in a very different way. Thus,

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[1] V. S. Vinogradov, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963* (Pergamon Press, Inc., New York, 1964).

[2] B. D. Silverman, Phys. Rev. **125**, 1921 (1962).

[3] G. Rupprecht and R. O. Bell, Phys. Rev. **125**, 1915 (1962).

[4] F. Jona and G. Shirane, *Ferroelectric Crystals* (Pergamon Press, Ltd., London, 1962).

for example, when substituting Sr or Pb ions for Ba ions in $BaTiO_3$, T_C decreases or increases, respectively, the change of T_C reaching several hundred degrees Kelvin (at 100% substitution). On the other hand the change of T_C when Ca ions are substituted for Ba ions is negligible.[4] The impurities present in the crystal lead also to changes in the lattice parameters. At the same time it is well known that with $BaTiO_3$ the Curie temperature can be decreased by hydrostatic pressure, revealing thus that T_C depends on the lattice constant. So the question arises whether the changes in T_C connected with the presence of impurities cannot be explained simply as a consequence of the change in the lattice constant. The case mentioned above shows, however, that this conclusion is not valid generally. The presence of Sr or Pb ions in $BaTiO_3$ leads to a decrease in the lattice constant. While Sr ions, in agreement with an influence of the hydrostatic pressure, decrease T_C, Pb ions, on the other hand, increase it.[4] It can be shown by similar consideration that one cannot find the direct connection between the changes of T_C and values of polarizability or radii of impurity ions.

Thus, to explain a change in the Curie temperature caused by defects, it is undoubtedly necessary to approach the more detailed characteristics of the defect on the basis of the interaction between the ions in the crystal, which is the aim of this paper. As has been stated, the polarizability of impurity ions is not a decisive factor governing the change in Curie temperature and we shall therefore regard crystal ions as nonpolarizable, which greatly simplifies our calculations. In the first part of this paper the method of time-dependent Green's functions[5] is used to derive a general expression for the susceptibility of an ionic crystal with defects. In the second part the result is specialized for the case of isovalent substitutional impurities in ferroelectric substances.

II. SUSCEPTIBILITY OF IONIC CRYSTAL WITH DEFECTS

We shall start with the Hamiltonian constructed similarly to the one in the paper by Vinogradov.[1] We shall, however, take into account the effect of the homogeneous deformation of the crystal. The influence of defects upon anharmonic coefficients will be neglected and therefore anharmonic terms in the expansion of the potential energy (in the displacements of the ions from their equilibrium positions in the defect crystal) will not be considered explicitly. In the first approximation, we shall express their contribution by the temperature dependence of harmonic coefficients of the ideal crystal and by its thermal expansion. In this way of course we cannot obtain the changes in the character of the temperature dependence of the dielectric constant. Particularly, we cannot obtain the slight change in the Curie constant of a defect ferroelectric crystal. This effect, however, is of less interest in comparison with the change of Curie temperature.

As follows from the Appendix, the Hamiltonian H equals

$$
\begin{aligned}
H=\text{const}+\sum_{\mathbf{y}j}\hbar\omega(\mathbf{y}j)a^\dagger(\mathbf{y}j)a(\mathbf{y}j)\\
+(\tfrac{1}{2}\hbar N)^{1/2}\sum_{\alpha\beta j}\omega^{-1/2}(\mathbf{0}j)\phi_{(\alpha\beta)}(--\mathbf{0}j)u_{\alpha\beta}A(\mathbf{0}j)\\
+\tfrac{1}{2}\hbar\sum_{\mathbf{y}j;\mathbf{y}'j'}B(\mathbf{y}j,\mathbf{y}'j')A(\mathbf{y}j)A(\mathbf{y}'j').
\end{aligned}
\tag{1}
$$

The creation and annihilation phonon operators satisfy the commutation relation

$$[a(\mathbf{y}j),a^\dagger(\mathbf{y}'j')]=\delta_{jj'}\delta_{\mathbf{y}\mathbf{y}'}.$$

All the operators A defined as

$$A(\mathbf{y}j)=a(\mathbf{y}j)+a^\dagger(-\mathbf{y}j)=A^\dagger(-\mathbf{y}j)$$

commute among themselves.

In the model of nonpolarizable ions the operator of the αth component of the dipole moment of the crystal M_α is

$$M_\alpha=\sum_{\mathbf{l}k}e(\mathbf{l}k)u_\alpha(\mathbf{l}k)=(\tfrac{1}{2}\hbar)^{1/2}\sum_{\mathbf{y}j}C_\alpha(\mathbf{y}j)A(\mathbf{y}j), \tag{2}$$

where $e(\mathbf{l}k)$ is the charge of the kth ion in the $\mathbf{l}$th unit cell and

$$
\begin{aligned}
C_\alpha(\mathbf{y}j)=[N\omega(\mathbf{y}j)]^{-1/2}\\
\times\textstyle\sum_k m_k^{-1/2}e_\alpha(k|\mathbf{y}j)\sum_{\mathbf{l}}e(\mathbf{l}k)e^{2\pi i\mathbf{y}\cdot\mathbf{x}(\mathbf{l})}.
\end{aligned}
\tag{3}
$$

The interaction energy of the crystal with the external homogeneous electric field $\mathbf{E}=\mathbf{E}_\omega e^{-i\omega t}$ is

$$H_{\text{int}}=-\textstyle\sum_\alpha M_\alpha E_\alpha.$$

Then, as is known from Ref. 5, the susceptibility $\chi_{\alpha\beta}(\omega)$ is given by the expression

$$\chi_{\alpha\beta}(\omega)=-(2\pi/Nv\hbar)G_R(\omega), \tag{4}$$

where v is the volume of the unit cell and where $G_R(\omega)$ is the ω Fourier component of the retarded Green's function $G_R(t-t')$ defined by the relation

$$
\begin{aligned}
G_R(t-t')=\int_{-\infty}^{+\infty}G_R(\omega)e^{-i\omega(t-t')}d\omega\\
=-i\Theta(t-t')\langle[M_\alpha(t),M_\beta(t')]\rangle_0.
\end{aligned}
\tag{5}
$$

$M_\alpha(t)$ is the Heisenberg operator for the αth component of the dipole moment, $\Theta(t-t')=1$ for $t>t'$ and $\Theta(t-t')=0$ for $t<t'$. The symbol $\langle\ \rangle_0$ denotes the statistical mean value for $\mathbf{E}=0$. We now introduce the retarded Green's function $G_{jj'}{}^{\mathbf{y}\mathbf{y}'}(t-t')$ by the relation

$$G_{jj'}{}^{\mathbf{y}\mathbf{y}'}(t-t')=-i\Theta(t-t')\langle[A(\mathbf{y}j,t),A(\mathbf{y}'j',t')]\rangle_0. \tag{6}$$

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[5] D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [English transl.: Soviet Phys.—Usp. **3**, 320 (1960)].

We then get from (4) using (2), (5), and (6)

$$\chi_{\alpha\beta}(\omega)=-(\pi/Nv)\sum_{\mathbf{y}\mathbf{y}';jj'}C_\alpha(\mathbf{y}j)C_\beta(\mathbf{y}'j')G_{jj'}{}^{\mathbf{y}\mathbf{y}'}(\omega)\,. \tag{7}$$

The following equations can easily be derived for the function $G_{jj'}{}^{\mathbf{y}\mathbf{y}'}(t-t')$ from the equations of motion for Heisenberg operators using the commutation relations for the operators a and A:

$$\begin{aligned}&i\partial G_{jj'}{}^{\mathbf{y}\mathbf{y}'}(t-t')/\partial t=-\omega(\mathbf{y}j)i\Theta(t-t')\langle[a(\mathbf{y}j,t)-a^\dagger(-\mathbf{y}j,\,t),A(\mathbf{y}'j',t')]\rangle_0\\&-\partial^2G_{jj'}{}^{\mathbf{y}\mathbf{y}'}(t-t')/\partial t^2=2\omega(\mathbf{y}j)\delta(t-t')\delta_{jj'}\delta_{\mathbf{y}_1-\mathbf{y}'}+\omega(\mathbf{y}j)\sum_{\mathbf{y}''j''}[2B(-\mathbf{y}j,\,\mathbf{y}''j'')+\omega(\mathbf{y}j)\delta_{jj''}\delta_{\mathbf{y}\mathbf{y}''}]G_{j''j'}{}^{\mathbf{y}''\mathbf{y}'}(t-t')\,.\end{aligned} \tag{8}$$

Using the Fourier transforms we obtain from (8)

$$\sum_{\mathbf{y}''j''}J_{jj''}{}^{\mathbf{y}\mathbf{y}''}G_{j''j'}{}^{\mathbf{y}''\mathbf{y}'}(\omega)=-\pi^{-1}\omega(\mathbf{y}j)\delta_{jj'}\delta_{\mathbf{y}_1-\mathbf{y}'}\,, \tag{9}$$

where

$$J_{jj'}{}^{\mathbf{y}\mathbf{y}'}=2\omega(\mathbf{y}j)B(-\mathbf{y}j,\,\mathbf{y}'j')+[\omega^2(\mathbf{y}j)-\omega^2]\delta_{jj'}\delta_{\mathbf{y}\mathbf{y}'}\,.$$

We shall now regard the pair of indices $\mathbf{y}$, j as one index and denote the inverse matrix to J by $H\equiv J^{-1}$. The solution of the system of equations for $G_{jj'}{}^{\mathbf{y}\mathbf{y}'}(\omega)$ then has the form

$$G_{jj'}{}^{\mathbf{y}\mathbf{y}'}(\omega)=-\pi^{-1}\omega(\mathbf{y}'j')H_{jj'}{}^{\mathbf{y}_1-\mathbf{y}'}(\omega)\,. \tag{10}$$

Note that, owing to the simple form of the Hamiltonian (1) (without anharmonic terms), we were able to find an exact expression for the Fourier transforms of the retarded Green's functions defining $\chi_{\alpha\beta}(\omega)$. The final expression for $\chi_{\alpha\beta}(\omega)$ is obtained from relations (7) and (10):

$$\chi_{\alpha\beta}(\omega)=(Nv)^{-1}\sum_{\mathbf{y}\mathbf{y}';jj'}C_\alpha(\mathbf{y}j)C_\beta(\mathbf{y}'j')\times\omega(\mathbf{y}'j')H_{jj'}{}^{\mathbf{y}_1-\mathbf{y}'}(\omega)\,. \tag{11}$$

In the model of nonpolarizable ions formula (11) expresses the susceptibility of the crystal with defects of a different type (e.g., substitutional ions of equal or different valence) in a homogeneous electric field.

The formula derived is exact but is of no practical significance since it assumes the solution generally of a system of $3Ns$ equations (s = number of ions in unit cell). We shall deal below only with the case of isovalent defects, when to express $\chi_{\alpha\beta}(\omega)$ it is enough to know only the Fourier transform of the retarded one-phonon Green's function $G_{jj}{}^{\mathbf{00}}(\omega)$. In this case, as follows from relations (2) and (3), only the optic modes $(\mathbf{0}j)$ interact directly with the external electric field and determine the induced polarization. Let us therefore find an approximative expression for $G_{jj}{}^{\mathbf{00}}(\omega)$.

From Eq. (9) we obtain for $G_{jj}{}^{\mathbf{00}}(\omega)$

$$[\omega^2-\omega^2(\mathbf{0}j)-2\omega(\mathbf{0}j)B(\mathbf{0}j,\mathbf{0}j)]G_{jj}{}^{\mathbf{00}}=(\omega(\mathbf{0}j)/\pi)[1+2\pi\sum_{(\mathbf{y}'j')\neq(\mathbf{0}j)}B(\mathbf{0}j,\mathbf{y}'j')G_{j'j}{}^{\mathbf{y}'\mathbf{0}}]\,. \tag{12}$$

In the first approximation we neglect the real scattering of the phonon $(\mathbf{0}j)$ on defects, i.e., we put all $B(\mathbf{0}j,\mathbf{y}'j')$ equal to zero for $(\mathbf{y}'j')\neq(\mathbf{0}j)$ and from relation (12) we obtain

$${}^{(1)}G_{jj}{}^{\mathbf{00}}(\omega)=-\frac{1}{\pi}\frac{\omega(\mathbf{0}j)}{\omega^2(\mathbf{0}j)+2\omega(\mathbf{0}j)B(\mathbf{0}j,\mathbf{0}j)-\omega^2}\,. \tag{13}$$

The influence of defects thus appears in this approximation only as a change in energy of the phonon. From (9) we now find an equation for $G_{j'j}{}^{\mathbf{y}'\mathbf{0}}$ in the form

$$\begin{aligned}&[\omega^2-\omega^2(\mathbf{y}'j')-2\omega(\mathbf{y}'j')B(-\mathbf{y}'j',\,\mathbf{y}'j')]G_{j'j}{}^{\mathbf{y}'\mathbf{0}}\\&\qquad=2\omega(\mathbf{y}'j')B(-\mathbf{y}'j',\,\mathbf{0}j)G_{jj}{}^{\mathbf{00}}+2\omega(\mathbf{y}'j')\sum_{(\mathbf{y}''j'')\neq(\mathbf{0}j),(\mathbf{y}'j')}B(-\mathbf{y}'j',\,\mathbf{y}''j'')G_{j''j}{}^{\mathbf{y}''\mathbf{0}}\,.\end{aligned} \tag{14}$$

In the next approximation we take into consideration only the scattering on defects of the phonon $(\mathbf{0}j)$, which interacts directly with the external field, and neglect the scattering of the other phonons, which in our case only indirectly influence the dielectric properties. Thus only the coefficients $B(-\mathbf{y}'j',\,\mathbf{0}j)$ will be nonzero. Using (14) and (12), we obtain

$${}^{(2)}G_{jj}{}^{\mathbf{00}}(\omega)=-\pi^{-1}\omega(\mathbf{0}j)\left[\omega^2(\mathbf{0}j)+2\omega(\mathbf{0}j)B(\mathbf{0}j,\mathbf{0}j)-\omega^2-4\sum_{(\mathbf{y}'j')\neq(\mathbf{0}j)}\frac{\omega(\mathbf{0}j)\omega(\mathbf{y}'j')|B(\mathbf{0}j,\mathbf{y}'j')|^2}{\omega^2(\mathbf{y}'j')+2\omega(\mathbf{y}'j')B(-\mathbf{y}'j',\,\mathbf{y}'j')-\omega^2}\right]^{-1}\,. \tag{15}$$

The determination of the poles of expression (15) in this case represents a very complicated problem and in general we can say that in this approximation we obtain a further change in energy of the phonon $(\mathbf{0}j)$ and its finite lifetime. Note that the energy shift is due to the virtual scattering of phonons, whereas their finite lifetime arises from real scattering.

By rewriting (10) it can easily be shown that the exact solution of $G_{jj}{}^{\mathbf{00}}(\omega)$ has the form

$$G_{jj}{}^{\mathbf{00}}(\omega)=-\frac{1}{\pi}\frac{\omega(\mathbf{0}j)}{\omega^2(\mathbf{0}j)+2\omega(\mathbf{0}j)B(\mathbf{0}j,\mathbf{0}j)-\omega^2+\sum_{(\mathbf{y}'j')\neq(\mathbf{0}j)}J_{jj'}{}^{\mathbf{0}\mathbf{y}'}\bar{J}_{jj'}{}^{\mathbf{0}\mathbf{y}'}(\omega)/\bar{J}_{jj}{}^{\mathbf{00}}(\omega)},$$

where $\bar{J}_{jj'}{}^{\mathbf{0}\mathbf{y}'}$ denotes the complement of the element $J_{jj'}{}^{\mathbf{0}\mathbf{y}'}$ of the matrix J.

When calculating $\chi_{\alpha\beta}(\omega)$ we shall content ourselves below with approximative expression (15) and rewrite it in the form (note that ω has a small positive imaginary part)

$$^{(2)}G_{jj}{}^{\mathbf{00}}(\omega)=-\frac{1}{\pi}\frac{\omega(\mathbf{0}j)}{\omega^2(\mathbf{0}j)+2\omega(\mathbf{0}j)[B(\mathbf{0}j,\mathbf{0}j)-\gamma_1(\omega)]-\omega^2+i\omega(\mathbf{0}j)\gamma_2(\omega)},\tag{16}$$

where

$$\gamma_1(\omega)=\sum_{(\mathbf{y}'j')\neq(\mathbf{0}j)}\frac{\omega(\mathbf{y}'j')\,|B(\mathbf{0}j,\mathbf{y}'j')|^2}{^{(1)}\omega(\mathbf{y}'j')}\left\{P\frac{1}{^{(1)}\omega(\mathbf{y}'j')+\omega}+P\frac{1}{^{(1)}\omega(\mathbf{y}'j')-\omega}\right\},$$

$$\gamma_2(\omega)=2\pi\sum_{(\mathbf{y}'j')\neq(\mathbf{0}j)}\frac{\omega(\mathbf{y}'j')\,|B(\mathbf{0}j,\mathbf{y}'j')|^2}{^{(1)}\omega(\mathbf{y}'j')}\{\delta(^{(1)}\omega(\mathbf{y}'j')+\omega)-\delta(^{(1)}\omega(\mathbf{y}'j')-\omega)\},\tag{16'}$$

and

$$^{(1)}\omega^2(\mathbf{y}'j')=\omega^2(\mathbf{y}'j')+2\omega(\mathbf{y}'j')B(-\mathbf{y}'j',\mathbf{y}'j').$$

III. INFLUENCE OF ISOVALENT IMPURITIES ON CURIE TEMPERATURE

The calculation of $\chi_{\alpha\beta}(\omega)$, of course, requires a knowledge of the forces between the ions in an ideal as well as a nonideal crystal. In this paper we shall not deal with the numerical calculations but shall confine ourselves to a qualitative discussion of the result in the special case of crystal defects, i.e., at the substitution of some ions by impurity ions of the same valency. In such a case, as follows from definition (3), only the coefficients $C_\alpha(\mathbf{0}j)$ are nonzero, while j relates to the optic modes of the phonon spectrum. We shall consider only one transverse optic branch (denoted by the index j), which is possible with crystals of the NaCl type and particularly with ferroelectric crystals in the paraelectric phase where the dielectric properties are determined mainly by one optic transverse mode with an anomalously low frequency in the neighborhood of the Curie temperature. At the same time it is known[4] that, for example in BaTiO$_3$ single crystals at the substitution of Ba ions by isovalent Sr or Pb ions, or Ti ions by Sn ions etc. (or similar substitution in PbTiO$_3$), the magnitude of the Curie temperature changes considerably without essentially changing the character of the temperature dependence of the dielectric constant, that is the Curie-Weiss law is valid with practically the same Curie constant.

Since the paraelectric phase of BaTiO$_3$ has cubic symmetry, we get in the above special case of crystal defects the following expression for the scalar quantity $\chi(\omega)$ using relations (7) and (16)

$$\chi(\omega)=\chi_{\alpha\alpha}(\omega)=-\frac{1}{v}\frac{M_\alpha{}^2(\mathbf{0}j)}{\omega^2(\mathbf{0}j)+2\omega(\mathbf{0}j)[B(\mathbf{0}j,\mathbf{0}j)-\gamma_1(\omega)]-\omega^2+i\omega(\mathbf{0}j)\gamma_2(\omega)},$$

where

$$M_\alpha(\mathbf{0}j)=[\omega(\mathbf{0}j)/N]^{1/2}C_\alpha(\mathbf{0}j)=\sum_k m_k{}^{-1/2}e_ke_\alpha(k|\mathbf{0}j).$$

After substituting for $B(\mathbf{0}j,\mathbf{0}j)$ from definition (A5) and using the fact that for centrosymmetrical crystals the coefficients $\phi(\mathbf{0}j,\mathbf{0}j',\mathbf{0}j'')$ vanish, we finally obtain for the static susceptibility χ

$$\chi=\frac{1}{v}\frac{M_\alpha{}^2(\mathbf{0}j)}{\omega^2(\mathbf{0}j)+\delta\phi(\mathbf{0}j,\mathbf{0}j)+\sum_{\alpha\beta}\phi_{(\alpha\beta)}(--\mathbf{0}j,\,\mathbf{0}j)u_{\alpha\beta}-2\omega(\mathbf{0}j)\gamma_1(0)}.\tag{17}$$

The static dielectric constant ϵ_s of ferroelectric crystals satisfies the Curie-Weiss law at temperatures higher than the Curie temperature T_C

$$\epsilon_s = C/(T-T_C).$$

As is known,[6] this law is the consequence of the temperature dependence of the frequency of the "ferroelectric" mode $\omega(\mathbf{0}j)$:

$$\omega^2(\mathbf{0}j) = \gamma(T-T_C).$$

Similarly as in papers,[7,8] such a temperature dependence would be obtained if the anharmonic terms in the potential-energy expansion (in ionic displacements) were accounted for explicitly. Entirely neglecting the changes of anharmonic coefficients due to defects (as well as other terms of the same order), γ and T_C will obviously have the same values as in an ideal crystal. Note that in this temperature dependence the contribution from the thermal expansion is already included; in the following $u_{\alpha\beta}$ will denote deformations due to external forces or defects only. According to (17) the Curie constant C of an ideal crystal in our model equals

$$C = 4\pi M_\alpha{}^2(\mathbf{0}j)/\gamma v$$

and ϵ_s of a nonideal crystal can thus, also using (17), be written in the form

$$\epsilon_s = C/(T-T_C'), \quad \text{where} \quad T_C' = T_C + \Delta T_C$$

and

$$\Delta T_C = -\gamma^{-1}\{\delta\phi(\mathbf{0}j,\mathbf{0}j) + \sum_{\alpha\beta} \phi_{\alpha\beta}(--\mathbf{0}j,\mathbf{0}j)u_{\alpha\beta} - 2\omega(\mathbf{0}j)\gamma_1(0)\}. \quad (18)$$

[Note that the last term in (18) does not in reality depend on the temperature-dependent frequency $\omega(\mathbf{0}j)$ as follows from (16′) and (A5).]

It is thus seen that the influence of defects on ϵ_s of a ferroelectric crystal in the paraelectric phase in our model and in approximation (15) is apparent only as a change in Curie temperature T_C of ΔT_C. In our approximation as it follows from (18) the shift of T_C is due to the change in the harmonic forces between ions when impurities are present. In fact only changes in short-range forces occur because the impurity ions are considered to be isovalent and nonpolarizable. Roughly speaking, at T_C the short-range restoring forces and the long-range Coulomb forces in the ferroelectric mode are nearly cancelled. Then a slight change in the short-range forces caused by defects leads to the shift of T_C. In the first approximation this shift is expressed through the first two terms in (18). The second one is in fact present only when the defects cause the homogeneous deformation (or when the external pressure is applied). Such a situation arises in the case of perovskites with various isovalent impurities as has already been stated. However, thanks to the first term in (18) the change in the lattice constant is not a decisive factor controlling the shift of T_C as is established experimentally. No change in the Curie constant is obtained as the influence of defects upon anharmonic coefficients was not considered. For the same reason neither is the influence of pressure upon T_C expressed in formula (18) by linear terms in $u_{\alpha\beta}$ changed.

Using relations (A6) ΔT_C can be rewritten in the form [the first two terms in (18)]

$$\Delta T_C = -\frac{1}{\gamma N} \sum_{\alpha k k'; \mathbf{l}\mathbf{l}'} \frac{e_\alpha(k|\mathbf{0}j) e_\alpha(k'|\mathbf{0}j)}{(m_k m_k{}')^{1/2}} \times \delta\phi_{\alpha\alpha}(\mathbf{l}k,\mathbf{l}'k') - \frac{1}{\gamma} u \sum_\alpha \phi_{(\alpha\alpha)}(--\mathbf{0}j,\mathbf{0}j), \quad (19)$$

where u denotes the relative change of the lattice constant.

Let us now study the dependence of ΔT_C on the number of randomly distributed defects n in a crystal. Since, for the type of defects considered, only the short-range forces between the ions change, it is obvious that the first term in (19) is nonzero only for those values of $\mathbf{l}'$ which denote the lattice positions in the immediate neighborhood of the defect at the position $\mathbf{l}$. At such a concentration of defects when the range of influence of the different defects is smaller than the average distance between them, we obtain n equal terms when summing over $\mathbf{l}$. In such a case the first term in (19) will be proportional to n/N i.e., the concentration of defects. As the linear concentration dependence of u is experimentally established, the shift of T_C will be proportional to the concentration of defects. Similar considerations show that even the last term in expression (18), expressing the Curie temperature shift in the next approximation, is proportional to the concentration of defects, if we neglect corresponding changes in "normal" frequencies. Since we consider the changes in the short-range forces only, it is clear from the above that a linear concentration dependence of the shift of the Curie point can be expected up to relatively high concentrations of substituted isovalent ions. Such a dependence was observed for example in systems such as (Ba,Sr)TiO_3, Ba(Ti,Sn)O_3, (Pb,Ca)TiO_3, (Pb,Sr)TiO_3 (Ref. 4) at least up to 30 mole% of admixture. On the other hand, in (Pb,Ba)TiO_3 and Ba(Ti,Zr)O_3 systems,[4] deviations from the linear dependence of ΔT_C on the concentration appear even at low concentrations and it might be necessary for their qualitative explanation to take into consideration changes of long-range forces caused by the different polarizability of the impurity ions. The calculation of the Curie temperature shift

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[6] W. Cochran, Advan. Phys. **9**, 387 (1960). A. S. Barker and M. Tinkham, Phys. Rev. **125**, 1527 (1962). R. A. Cowley, Phys. Rev. Letters **9**, 159 (1962).

[7] R. A. Cowley, Advan. Phys. **12**, 421 (1963). B. D. Silverman and R. I. Joseph, Phys. Rev. **129**, 2062 (1963). R. A. Cowley, Phil. Mag. **11**, 673 (1965).

[8] M. A. Krivoglaz, Zh. Eksperim. i Teor. Fiz. **40**, 567 (1961) [English transl.: Soviet Phys.—JETP **13**, 397 (1961)].

ΔT_C using Eq. (18) requires a detailed knowledge of the force constants between the ions and is therefore not a very hopeful method at present. In principle, however, it should explain the different signs of ΔT_C, e.g., in $BaTiO_3$, when Ba ions are substituted by Sr and Pb ions, the negligible shift of T_C when Ba ions are substituted by Ca ions,[4] etc. Considerations of this kind will be the subject of a later paper.

As a consequence of changes in the phonon spectrum, the influence of defects is apparent even on inelastic scattering of neutrons through a defect crystal. (These questions are discussed in detail in Ref. 8.) This problem is particularly interesting in ferroelectric materials with an anomalously low frequency of the ferroelectric mode, where a considerable relative change in this frequency is expected as a result of defects. It must be stressed that, strictly speaking, it is only in the first approximation (13) that we can interpret the Curie temperature shift as a change in frequency of the ferroelectric mode and on the basis of this estimate its relative change $\Delta\omega(\mathbf{0}j)/\omega(\mathbf{0}j)$. Using the temperature dependence $\omega^2(\mathbf{0}j)=\gamma(T-T_C)$, we obtain

$$\Delta\omega(\mathbf{0}j)/\omega(\mathbf{0}j)=[1-\Delta T_C/(T-T_C)]^{1/2}-1\,.$$

From the requirement that the temperature T correspond to the paraelectric phase of an ideal and a nonideal crystal, we obtain the condition

$$T-T_C>0\,,\quad T-T_C>\Delta T_C\,.$$

For example, for a concentration of 30 mole% Sr in $BaTiO_3$,[4] $\Delta T_C \simeq -100$°K, and at a temperature 20°K higher than T_C of pure $BaTiO_3$, it will hold that $\Delta\omega(\mathbf{0}j)/\omega(\mathbf{0}j)\simeq 1.4$. On the other hand, when substituting Ba ions for Sr ions in $SrTiO_3$ the frequency $\omega(\mathbf{0}j)$ will decrease; for example, at a concentration of 10 mole% Ba we have[4] $\Delta T_C \simeq 40$°K and at a temperature $T=90$°K, $\Delta\omega(\mathbf{0}j)/\omega(\mathbf{0}j)=-0.4$. Such changes could easily be measured.

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APPENDIX

As in Ref. 1, let us write the potential energy U of a crystal in the form

$$U=\phi+\delta\phi\,,$$

where ϕ is the potential energy of the ideal crystal and $\delta\phi$ its change caused by the presence of defects. The quantity U is expanded only into terms quadratic in the displacements $\mathbf{u}(\mathbf{l}k)$ of the ions from the positions $\mathbf{X}(\mathbf{l}k)$ defined as

$$\mathbf{X}(\mathbf{l}k)=\mathbf{X}^0(\mathbf{l}k)+\mathbf{v}(\mathbf{l}k)+\mathbf{d}(\mathbf{l}k)\,.$$

$\mathbf{X}^0(\mathbf{l}k)$ denotes the position vector of the kth ion in the $\mathbf{l}$th unit cell of the ideal lattice at $T=0$°K and $\mathbf{v}(\mathbf{l}k)$ its change due to defects. $\mathbf{d}(\mathbf{l}k)$ expresses the deformation due to the thermal expansion or (for example) hydrostatic pressure and we shall write it in the form

$$d_\alpha(\mathbf{l}k)=\sum_\beta u_{\alpha\beta}[X_\beta{}^0(\mathbf{l}k)+v_\beta(\mathbf{l}k)]\,.$$

$$U=\text{const}+\sum_{\alpha\mathbf{l}k}\frac{\partial(\phi+\delta\phi)}{\partial X_\alpha(\mathbf{l}k)}\bigg|_{\mathbf{X}}u_\alpha(\mathbf{l}k)+\tfrac{1}{2}\sum_{\substack{\alpha\mathbf{l}k\\ \beta\mathbf{l}'k'}}\frac{\partial^2(\phi+\delta\phi)}{\partial X_\alpha(\mathbf{l}k)\partial X_\beta(\mathbf{l}'k')}\bigg|_{\mathbf{X}}u_\alpha(\mathbf{l}k)u_\beta(\mathbf{l}'k')\,. \tag{A1}$$

Now let us expand the derivatives in points $\mathbf{X}$ in a Taylor series in powers of $\mathbf{d}$ about $\mathbf{X}^0+\mathbf{v}$ and then in powers of $\mathbf{v}$ about $\mathbf{X}^0$. Using the conditions

$$\frac{\partial(\phi+\delta\phi)}{\partial X_\alpha{}^0(\mathbf{l}k)}\bigg|_{\mathbf{X}^0+\mathbf{v}}=0 \tag{A2}$$

which determine the displacements $\mathbf{v}$ due to defects and by confining ourselves to the first terms of this expansion, we obtain (see Ref. 9)

$$\begin{aligned}\frac{\partial(\phi+\delta\phi)}{\partial X_\alpha(\mathbf{l}k)}\bigg|_{\mathbf{X}}&=\sum_{\beta\mathbf{l}'k'}\phi_{\alpha\beta}(\mathbf{l}k,\mathbf{l}'k')d_\beta(\mathbf{l}'k')\,,\\ \frac{\partial^2(\phi+\delta\phi)}{\partial X_\alpha(\mathbf{l}k)\partial X_\beta(\mathbf{l}'k')}\bigg|_{\mathbf{X}}&=\phi_{\alpha\beta}(\mathbf{l}k,\mathbf{l}'k')+\delta\phi_{\alpha\beta}(\mathbf{l}k,\mathbf{l}'k')+\sum_{\gamma\mathbf{l}''k''}\phi_{\alpha\beta\gamma}(\mathbf{l}k,\mathbf{l}'k',\mathbf{l}''k'')[v_\gamma(\mathbf{l}''k'')+d_\gamma(\mathbf{l}''k'')]\,,\end{aligned} \tag{A3}$$

where all second-order terms in $\delta\phi$, $\mathbf{v}$, and $u_{\alpha\beta}$ are neglected.

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[9] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954).

By neglecting the changes in mass connected with the crystal defects which do not influence the static dielectric constant, the kinetic energy T is

$$T=\tfrac{1}{2}\sum_{\alpha\mathbf{l}k} m_k\dot{u}_\alpha^2(\mathbf{l}k)\,.$$

Expressing $u_\alpha(\mathbf{l}k)$ by means of the creation and annihilation photon operators as

$$u_\alpha(\mathbf{l}k)=\left(\frac{\hbar}{2Nm_k}\right)^{1/2}\sum_{\mathbf{y}j}\omega^{-1/2}(\mathbf{y}j)e_\alpha(k\,|\,\mathbf{y}j)e^{2\pi i\mathbf{y}\cdot\mathbf{x}(\mathbf{l})}[a(\mathbf{y}j)+a^\dagger(-\mathbf{y}j)]\,,\tag{A4}$$

the Hamiltonian of the nonideal crystal will have the form

$$H=\text{const}+\sum_{\mathbf{y}j}\hbar\omega(\mathbf{y}j)a^\dagger(\mathbf{y}j)a(\mathbf{y}j)+\left(\frac{\hbar N}{2}\right)^{1/2}\sum_{\alpha\beta j}\omega^{-1/2}(\mathbf{0}j)\phi_{(\alpha\beta)}(--\mathbf{0}j)u_{\alpha\beta}A(\mathbf{0}j)+\frac{\hbar}{2}\sum_{\mathbf{y}j;\mathbf{y}'j'}B(\mathbf{y}j,\mathbf{y}'j')A(\mathbf{y}j)A(\mathbf{y}'j')\,.$$

Note that in our approximation the terms linear in A do not influence the expression for the susceptibility. Using (A1), (A3), and (A4) we obtain for $B(\mathbf{y}j,\mathbf{y}'j')$,

$$\begin{aligned}B(\mathbf{y}j,\mathbf{y}'j')=\tfrac{1}{2}[\omega(\mathbf{y}j)\omega(\mathbf{y}'j')]^{-1/2}\{\delta\phi(\mathbf{y}j,\mathbf{y}'j')+N^{-1/2}\sum_{\mathbf{y}''j''}\Delta(\mathbf{y}+\mathbf{y}'+\mathbf{y}'')\\ \times\phi(\mathbf{y}j,\mathbf{y}'j',\mathbf{y}''j'')q(\mathbf{y}''j'')+\Delta(\mathbf{y}+\mathbf{y}')\sum_{\alpha\beta}\phi_{(\alpha\beta)}(--\mathbf{y}j,\,\mathbf{y}'j')u_{\alpha\beta}\}\,,\end{aligned}\tag{A5}$$

where

$$\begin{aligned}q(\mathbf{y}j)&=N^{-1/2}\sum_{\alpha\mathbf{l}k}m_k^{1/2}v_\alpha(\mathbf{l}k)e_\alpha^*(k\,|\,\mathbf{y}j)e^{-2\pi i\mathbf{y}\cdot\mathbf{x}(\mathbf{l})}\,,\\ \delta\phi(\mathbf{y}j,\mathbf{y}'j')&=N^{-1}\sum_{\substack{\alpha\mathbf{l}k\\ \beta\mathbf{l}'k'}}\delta\phi_{\alpha\beta}(\mathbf{l}k,\mathbf{l}'k')(m_km_{k'})^{-1/2}e_\alpha(k\,|\,\mathbf{y}j)e_\beta(k'\,|\,\mathbf{y}'j')\exp2\pi i[\mathbf{y}\cdot\mathbf{x}(\mathbf{l})+\mathbf{y}'\cdot\mathbf{x}(\mathbf{l}')]\,,\\ \phi(\mathbf{y}j,\mathbf{y}'j',\mathbf{y}''j'')&=\sum_{\substack{\alpha k\\ \beta\mathbf{l}'k'\\ \gamma\mathbf{l}''k''}}\phi_{\alpha\beta\gamma}(\mathbf{0}k,\mathbf{l}'k',\mathbf{l}''k'')(m_km_{k'}m_{k''})^{-1/2}\\ &\qquad\times e_\alpha(k\,|\,\mathbf{y}j)e_\beta(k'\,|\,\mathbf{y}'j')e_\gamma(k''\,|\,\mathbf{y}''j'')\exp2\pi i[\mathbf{y}'\cdot\mathbf{x}(\mathbf{l}')+\mathbf{y}''\cdot\mathbf{x}(\mathbf{l}'')]\,,\\ \phi_{(\alpha\beta)}(--\mathbf{y}j,\,\mathbf{y}'j')&=\sum_{\substack{\mu\nu\\ \bar{\mathbf{l}}\bar{k}\\ k\mathbf{l}'k'}}\phi_{\alpha\mu\nu}(\bar{\mathbf{l}}\bar{k},\mathbf{0}k,\mathbf{l}'k')X_\beta{}^0(\bar{\mathbf{l}}\bar{k})(m_km_{k'})^{-1/2}e_\mu(k\,|\,\mathbf{y}j)e_\nu(k'\,|\,\mathbf{y}'j')\exp[2\pi i\mathbf{y}'\cdot\mathbf{x}(\mathbf{l}')]\,.\end{aligned}\tag{A6}$$

It can easily be shown that

$$B(\mathbf{y}j,\mathbf{y}'j')=B(\mathbf{y}'j',\mathbf{y}j)=B^*(-\mathbf{y}j,\,-\mathbf{y}'j')\,.$$