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## On the Influence of Conduction Electrons on the Ferroelectric Curie Temperature

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The frequency dependence of the transverse optical mode in the long-wavelength limit on the density of conduction electrons is calculated. This dependence is a consequence of the dielectric properties of the free electron gas which gives a change of the effective ion-ion interaction. By putting the limiting frequency equal to zero one finds an equation for the ferroelectric Curie temperature.

Es wird die Frequenzabhängigkeit der transversalen optischen Gitterschwingungen von der Dichte der Leitungselektronen im Grenzfall langer Wellen berechnet. Diese Abhängigkeit folgt aus den dielektrischen Eigenschaften des freien Elektronengases, die eine Änderung der Ion-Ion Wechselwirkung ergeben. Es läßt sich eine Formel für die ferroelektrische Curietemperatur finden, wenn man die Grenzfrequenz gleich Null setzt.

### 1. Introduction

In the years since 1959 several publications [1 to 4] appeared in which phonon dispersion curves, measured with neutron spectroscopy, were compared with theoretical calculations based on a rigid ion and a shell model. In 1960 Cochran [5, 6] showed that the ferroelectric transition in ionic crystals arises from instabilities of these crystals against a normal mode of vibration. As a function of temperature the limiting frequency of the transverse optical mode becomes zero at the Curie point, as expressed by the Lyddane-Sachs-Teller relation [5, 7, 8]. Later interest was in the lattice dynamics of ferroelectric semiconductors as PbS, PbTe, and SnTe, in which the measurement of the static dielectric constant and the Curie temperature are difficult because of the high conductivity [9 to 13]. In connection with the work on SbSI and FeS in our laboratory [14] the following problem arose: What is the dependence of the Curie temperature on the concentration of charge carriers? This problem will be analysed in this paper on the basis of a simple model for the coupled ion-electron system.

We will consider a lattice consisting of two types of ions immersed in an electron gas. The ions interact with one another via Coulomb forces and via central repulsive forces. The electrons screen the ions as a consequence of the Coulomb interaction between ions and electrons. From the expression for the screened Coulomb potential the limiting frequency of the transverse optical mode is calculated and by putting this frequency equal to zero we get the Curie temperature as a function of the electron density.

As a general conclusion we may state that this temperature decreases with increasing electron concentration. An approximate expression is given for the shift of this temperature.

To the authors' knowledge no experimental results have been reported on the relation between the ferroelectric Curie temperature and the electron density in samples of SbSI. For Fe<sub>1-x</sub>S Hirahara and Murakami [15] have observed a decrease in the  $\alpha$ -transition temperature with increasing conductivity. If this transition temperature is identified as a ferroelectric transition temperature [16] these results are in qualitative agreement with ours.

## 2. Effective Force between the Screened Ions

The potential field of the bare ions is given by

$$V(\mathbf{r}) = \sum_i \frac{Z_i e}{|\mathbf{r} - \mathbf{R}_i|}, \quad (1)$$

where  $Z_i e$  is the charge and  $\mathbf{R}_i$  the position of the  $i$ -th ion.

For the effective potential of the screened  $i$ -th ion we take

$$W_i(\mathbf{r}) = \frac{Z_i e}{|\mathbf{r} - \mathbf{R}_i|} \exp(-\lambda |\mathbf{r} - \mathbf{R}_i|), \quad (2)$$

where (see Ziman [17])

$$\lambda^2 = 4\pi e^2 N(E_F) = \frac{6\pi e^2 n_0}{kT_F} \quad (3a)$$

for a degenerate electron gas with density  $n_0$  and

$$\lambda^2 = \frac{4\pi e^2 n_0}{kT} \quad (3b)$$

for a classical electron gas with density  $n_0$ .

The energy of two ions at  $\mathbf{R}_i$  and  $\mathbf{R}_j$  is given by

$$E(\mathbf{R}_i, \mathbf{R}_j) = \frac{Z_i Z_j e^2}{|\mathbf{R}_i - \mathbf{R}_j|} \exp(-\lambda |\mathbf{R}_i - \mathbf{R}_j|), \quad (4)$$

and the total screened Coulomb energy is

$$E_{\text{tot}} = \frac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} E(\mathbf{R}_i, \mathbf{R}_j) \equiv \frac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} E(R_{ij}) \quad (5)$$

with  $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$  and  $R_{ij} = |\mathbf{R}_{ij}|$ .

For the force on the  $l$ -th ion we can write

$$\mathbf{K}_l = -\nabla_{\mathbf{R}_l} E_{\text{tot}} = -\sum_{\substack{j \\ (j \neq l)}} \frac{\partial E}{\partial R_{lj}}(R_{lj}) \frac{\mathbf{R}_{lj}}{R_{lj}} \quad (6)$$

with

$$E(R_{lj}) = \frac{Z_l Z_j e^2}{R_{lj}} \exp(-\lambda R_{lj}). \quad (7)$$

## 3. Series Expansion of the Force

We define

$$\begin{aligned} \mathbf{R}_i &= \mathbf{R}_i^0 + \delta\mathbf{R}_i, \\ \mathbf{R}_{ij}^0 &= \mathbf{R}_i^0 - \mathbf{R}_j^0, \\ \mathbf{R}_{ij} &= \mathbf{R}_{ij}^0 + \delta\mathbf{R}_{ij}, \end{aligned}$$

where  $\mathbf{R}_i^0$  is the equilibrium position of the  $i$ -th ion.

Next we expand the force  $\mathbf{K}_l$  from (6) in powers of  $\delta\mathbf{R}_{jl}$  and get the following result:

$$\begin{aligned} \mathbf{K}_l = - \sum_j \left[ - \frac{\partial E}{\partial R_{jl}} (R_{jl}^0) \frac{\mathbf{R}_{jl}^0}{R_{jl}^0} - \frac{\partial^2 E}{\partial R_{jl}^2} (R_{jl}^0) \times \right. \\ \times \frac{\mathbf{R}_{jl}^0 \cdot \delta\mathbf{R}_{jl}}{(R_{jl}^0)^2} \mathbf{R}_{jl}^0 - \frac{\partial E}{\partial R_{jl}} (R_{jl}^0) \frac{\delta\mathbf{R}_{jl}}{R_{jl}^0} + \\ \left. + \frac{\partial E}{\partial R_{jl}} (R_{jl}^0) \frac{\mathbf{R}_{jl}^0 \cdot \delta\mathbf{R}_{jl}}{(R_{jl}^0)^3} \mathbf{R}_{jl}^0 \right]. \end{aligned} \quad (8)$$

From (7) we calculate

$$\frac{\partial E}{\partial R_{jl}} (R_{jl}^0) = - Z_l Z_j e^2 \frac{\lambda R_{jl}^0 + 1}{(R_{jl}^0)^2} \exp(-\lambda R_{jl}^0), \quad (9)$$

$$\frac{\partial^2 E}{\partial R_{jl}^2} (R_{jl}^0) = Z_l Z_j e^2 \frac{\lambda^2 (R_{jl}^0)^2 + 2\lambda R_{jl}^0 + 2}{(R_{jl}^0)^3} \exp(-\lambda R_{jl}^0). \quad (10)$$

The force  $\mathbf{K}_l$  vanishes for  $\delta\mathbf{R}_{jl}^0 = 0$ , so the first term in the sum (8) drops out. Substitution of (9) and (10) into (8) gives

$$\begin{aligned} \mathbf{K}_l = \sum_j \left[ - Z_l Z_j e^2 \frac{\lambda R_{jl}^0 + 1}{(R_{jl}^0)^3} \exp(-\lambda R_{jl}^0) \delta\mathbf{R}_{jl} + \right. \\ \left. + Z_l Z_j e^2 \frac{\lambda^2 (R_{jl}^0)^2 + 3\lambda R_{jl}^0 + 3}{(R_{jl}^0)^5} \exp(-\lambda R_{jl}^0) (\mathbf{R}_{jl}^0 \cdot \delta\mathbf{R}_{jl}) \mathbf{R}_{jl}^0 \right], \end{aligned} \quad (11)$$

We can write  $\mathbf{K}_l = Z_l e \mathbf{F}_l$ , where  $\mathbf{F}_l$  is the local effective electrical field at  $\mathbf{R}_l$ :

$$\begin{aligned} \mathbf{F}_l = \sum_j \left[ - Z_j e \frac{\lambda R_{jl}^0 + 1}{(R_{jl}^0)^3} \exp(-\lambda R_{jl}^0) \delta\mathbf{R}_{jl} + \right. \\ \left. + Z_j e \frac{\lambda^2 (R_{jl}^0)^2 + 3\lambda R_{jl}^0 + 3}{(R_{jl}^0)^5} \exp(-\lambda R_{jl}^0) (\mathbf{R}_{jl}^0 \cdot \delta\mathbf{R}_{jl}) \mathbf{R}_{jl}^0 \right]. \end{aligned} \quad (12)$$

#### 4. The Transverse Optical Mode

We now want to calculate  $\mathbf{F}_l$  for a transverse optical mode in a lattice consisting of two types of ions. We take

$$\delta\mathbf{R}_{i+} = \delta\mathbf{R}_+^0 \exp(i\mathbf{K} \cdot \mathbf{R}_i),$$

$$\delta\mathbf{R}_{i-} = \delta\mathbf{R}_-^0 \exp(i\mathbf{K} \cdot \mathbf{R}_i)$$

for the amplitudes of the positive and negative ions.  $\delta\mathbf{R}_+^0$  is parallel with  $\delta\mathbf{R}_-^0$  and both are perpendicular to  $\mathbf{K}$ .

We are interested in the limit  $\mathbf{K} \rightarrow 0$ . The sum for  $\mathbf{F}_l$  (equation (12)) is uniformly convergent for  $\lambda \neq 0$  because of the occurrence of the factor  $\exp(-\lambda R_{jl}^0)$ :

$$\lim_{\mathbf{K} \rightarrow 0} \sum_j \dots = \sum_j \lim_{\mathbf{K} \rightarrow 0} \dots,$$

and we may substitute

$$\delta\mathbf{R}_{i+} = \delta\mathbf{R}_+^0,$$

$$\delta\mathbf{R}_{i-} = \delta\mathbf{R}_-^0.$$

The field at a positive ion consists of two parts, one part corresponding to all the other positive ions and a second part corresponding to the negative ions. In the contributions of the positive ions there appears the quantity

$$\delta\mathbf{R}_{jl} \equiv \delta\mathbf{R}_j - \delta\mathbf{R}_l = \delta\mathbf{R}_+^0 - \delta\mathbf{R}_+^0 = 0,$$

and this means that the positive ions do not give a contribution to the field at a positive ion site in the limit of infinitely long waves.

The electrical field at a positive ion site  $\mathbf{R}_i$  reduces to

$$\begin{aligned} \mathbf{F}(\mathbf{R}_i, +) = \sum_j' \left[ -Z_- e \frac{\lambda R_{jl}^0 + 1}{(R_{jl}^0)^3} \exp(-\lambda R_{jl}^0) \times \right. \\ \times (\delta \mathbf{R}_+^0 - \delta \mathbf{R}_-^0) + Z_- e \frac{\lambda^2 (R_{jl}^0)^2 + 3\lambda R_{jl}^0 + 3}{(R_{jl}^0)^5} \times \\ \left. \times (\mathbf{R}_{jl}^0 \cdot (\delta \mathbf{R}_+^0 - \delta \mathbf{R}_-^0)) \mathbf{R}_{jl}^0 \right]. \end{aligned} \quad (13)$$

$\sum_j'$  indicates a sum for all negative ion sites. We now take as our lattice a NaCl structure and calculate (13) by substituting

$$\mathbf{R}_{jl}^0 = a \begin{pmatrix} n \\ m \\ p \end{pmatrix},$$

where  $2a$  is the lattice constant and  $n$ ,  $m$ , and  $p$  are integers. It can be shown that for a NaCl structure the sum over the negative ions can be written as

$$\sum_j' = \sum_{\substack{n, m, p \\ n+m+p = \text{odd}}}.$$

After some calculation we get for the field at a positive ion

$$\mathbf{F}(+) = \frac{4\pi}{3} n Z_- e (\delta \mathbf{R}_+^0 - \delta \mathbf{R}_-^0) G(\lambda a), \quad (14)$$

where

$$n = \frac{4}{(2a)^3}$$

and

$$G(x) = \frac{1}{2\pi} \sum_{\substack{n, m, p \\ n+m+p = \text{odd}}} \frac{x^2}{(n^2 + m^2 + p^2)^{1/2}} \exp(-x(n^2 + m^2 + p^2)^{1/2}). \quad (15)$$

In an analogous way we have

$$\mathbf{F}(-) = \frac{4\pi}{3} n Z_+ e (\delta \mathbf{R}_+^0 - \delta \mathbf{R}_-^0) G(\lambda a). \quad (16)$$

In connection with the formulas (14), (15), and (16) we can make the following remarks:

(i) For  $\lambda = 0$  (no conduction electrons) the derivation is no longer correct because the sum is not uniformly convergent and the interchange of summation and taking the limit is not allowed.

(ii) The function  $G(x)$  has the limiting value 1 for  $x \rightarrow 0$ .

(iii) If we define  $G(0) = 1$  we can also use (14) and (15) for the case  $\lambda = 0$ , for then we get

$$\mathbf{F}(+) = \frac{4\pi}{3} n Z_- e (\delta \mathbf{R}_-^0 - \delta \mathbf{R}_+^0) = \frac{4\pi}{3} \mathbf{P}.$$

(iv) For an electron density  $n_0 = 10^{18} \text{ cm}^{-3}$ , a lattice constant  $2a = 6 \text{ \AA}$ , and  $T = 300 \text{ }^\circ\text{K}$  we find  $x = 0.25$  by using formula (3b).

Table 1

 Numerical values of the function  $G(x)$ 

$x$	$G(x)$	$x$	$G(x)$
0.1	0.99913	0.6	0.96937
0.2	0.99654	0.7	0.95859
0.3	0.99223	0.8	0.94633
0.4	0.98624	0.9	0.93268
0.5	0.97860	1.0	0.91770

(v) For  $x = 0.1, 0.2, \dots, 1$  the numerical calculated values of  $G(x)$  are given in Table 1.

### 5. The Change of the Curie Temperature

The equations of motion for the ions are

$$\begin{aligned}
 -m_{\pm} \omega_{\mp}^2 \delta \mathbf{R}_{\pm}^0 &= K_{\text{cr}} (\delta \mathbf{R}_{\mp}^0 - \delta \mathbf{R}_{\pm}^0) + \\
 &+ \frac{4\pi}{3} n Z_- Z_+ e^2 G(\lambda a) (\delta \mathbf{R}_{\mp}^0 - \delta \mathbf{R}_{\pm}^0), \quad (17)
 \end{aligned}$$

where  $K_{\text{cr}}$  is the central repulsive force constant. The solution of the equations (17) is

$$\frac{m_+ m_-}{m_+ + m_-} \omega_{\mp}^2 = K_{\text{cr}} + \frac{4\pi}{3} n Z_- Z_+ e^2 G(\lambda a). \quad (18)$$

The ferroelectric Curie temperature is reached if  $\omega_{\mp}^2(T) = 0$ ; so we get the following equations for this transition temperature: equation (19) corresponds to the case of no electrons present and (20) with the case of finite density of conduction electrons:

$$\left[ K_{\text{cr}} + \frac{4\pi}{3} n Z_- Z_+ e^2 \right]_{T=T_c} = 0, \quad (19)$$

$$\left[ K_{\text{cr}} + \frac{4\pi}{3} n Z_- Z_+ e^2 G(\lambda a) \right]_{T=T'_c} = 0. \quad (20)$$

In formula (20)  $G(\lambda a)$  depends on  $T$  because  $\lambda$  (cf. formulae (3a) and (3b)) and  $a$  are functions of the temperature.

For the calculation of  $T'_c$  from equation (20) it is necessary that the dependence of  $K_{\text{cr}}$  from  $T$  is known. We calculate this dependence by using the following relations which apply for the case that there are no conduction electrons present<sup>1)</sup>:

$$\mu \omega_{\text{T}}^2 = K_{\text{cr}} + \frac{4\pi}{3} n Z_- Z_+ e^2,$$

$$\mu \omega_{\text{L}}^2 = K_{\text{cr}} - \frac{8\pi}{3} n Z_- Z_+ e^2,$$

$$\frac{\varepsilon_0}{\varepsilon_{\infty}} = \frac{\omega_{\text{L}}^2}{\omega_{\text{T}}^2},$$

$$\varepsilon_0 = \varepsilon_{\infty} + \frac{4\pi C}{T - T'_c}.$$

<sup>1)</sup> Cf. reference [5], pages 391 to 395.

The first and second equation give the frequency of the transverse and longitudinal optical modes. The third one is the Lyddane-Sachs-Teller relation and the last one is the Curie-Weiss law. In the case considered in this paper  $\epsilon_\infty = 1$  because the ions are not polarizable. From these equations we derive a relation between  $K_{cr}$  and  $T$  which depends on the parameter  $C$  and  $T_c$ :

$$K_{cr} = -\frac{4\pi}{3} Z_- Z_+ e^2 n \left( \frac{3}{4\pi C} (T - T_c) + 1 \right). \quad (21)$$

If we assume that  $n = 4/(2a)^3$  as a function of  $T$  is the same in both equations (19) and (20) we can substitute (21) into (20) and get the following relation for  $T'_c$ :

$$T'_c = T_c - \frac{4\pi C}{3} (1 - G(\lambda a)|_{T=T'_c}). \quad (22)$$

This equation is solved by means of iteration; the zero-order solution is found by taking  $T'_c = T_c$  in the right member of (22). We also may solve (22) by graphical methods.

In general we may state that for increasing concentration of charge carriers the Curie temperature decreases because  $dG(x)/dx < 0$ .

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