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Temperature Dependence of Magnetic Susceptibility

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Zusammenfassung. Der in der vorangehenden Arbeit[1]) abgeleitete Ausdruck für die Suszeptibilität genügt nicht zur Erklärung einer bei einigen Halbleitern im Bereich mässig tiefer Temperaturen gemessenen Temperaturabhängigkeit. Hier wird der Rahmen der Theorie erweitert durch Heranziehung der Elektron-Phonon Wechselwirkung. Diese gibt zu einer zusätzlichen Suszeptibilität Anlass, welche zwar hier nicht explizit berechnet wird, von der jedoch plausibel gemacht wird, dass sie den Effekt erklärt.

1. Introduction

The temperature dependence of the formulae (4.9–13) derived in the previous paper[1]) (all quotations of the type (4.9) refer to this paper) is governed by the Fermi distribution $f(E)$ and by the function $G(E_n, E_{n'})$. Although the result (4.14) is likely to account for the $\chi - T$ dependence of many crystals, anomalous behaviour is empirically found for some semiconductors. These substances show a diamagnetic susceptibility of the form

$$\chi_{exp} \cong -a + b\,T; \quad b > 0 \tag{1}$$

at moderately low temperatures where the density of conduction carriers is practically zero[2]). Since in the region of validity of (1) the minimum $|E_g - \zeta|$ of the energy difference $|E_n(\boldsymbol{k}) - \zeta|$ is of the order of about $20 \cdot kT$ the total susceptibility (4.14) there is of the form

$$\chi \cong \chi_0 + \chi_1(T)\, e^{-(E_g - \zeta)/k\,T}$$

where χ_0 is independent of T. Because of the factor exp $(-(E_g - \zeta)/kT)$ the second term in the latter formula is practically zero simultanously with the density of conduction carriers. Therefore our formula for χ does not account for the behaviour (1).

Some time ago an explanation for such an anomalous temperature dependence was proposed by KRUMHANSL and BROOKS[3]). According to these authors a van Vleck magnetism of the form (4.22) should be of importance, the leading term being one which connects valence and conduction band states. In their proposal the behaviour (1) is due to a temperature variation of the energy denominator which for the states in

question is well known empirically. It was pointed out earlier[4]), however, that from the point of view of a more general theory the justification for picking out this special term (4.22) is not convincing. Moreover, the temperature dependence assumed by KRUMHANSL and BROOKS is of a rather special nature. In fact, the variation of the energy gap between valence and conduction band as function of temperature has long previously been explained by FAN and others[5]) as a second order effect of the electron-phonon interaction. Therefore a more rigorous theory of the anamlous behaviour (1) would have to develop from this interaction. In what follows we shall develop the general lines of such a theory without, however, entering into a detailed calculation. It will become clear, at least in tight binding approximation, that a new type of function of T, different from those occuring in eqs. (4.9–13) comes into play, which qualitatively may well account for (1).

2. Statistics of the electron-phonon system

Since we are interested only in statistical effects of the electron-phonon interaction a second quantisation point of view is appropriate for the whole system.

The basic electronic states without electron-phonon interaction are the eigenstates $|k)$ of the Hamiltonian $\mathfrak{H}$ with a magnetic field present, eq. (2.3),

$$\mathfrak{H}\,|k) = W_k\,|k) \tag{2}$$

Then the second quantized electron Hamiltonian is

$$\mathfrak{H}_{EL} = \sum_k N_k\, W_k \tag{3}$$

where

$$N_k = a_k^*\, a_k \tag{4}$$

is the occupation number of electrons in state $|k)$, $N_k = 0$ or 1, and a_k^*, a_k are emission and absorption operators obeying the anticomutation rule

$$\{a_k,\, a_{k'}^*\} = \delta_{kk'} \tag{5}$$

The phonon amplitude at the lattice site $\boldsymbol{R}_\alpha$ we write as (the lattice is supposed here to be of Bravais type)

$$\boldsymbol{u}_\alpha(t) = (2\,G\,M)^{-\frac{1}{2}} \sum_q \omega_q{}^{-\frac{1}{2}}\, \boldsymbol{e}_q\, b_q\, e^{i(\boldsymbol{q}\boldsymbol{R}_\alpha - \omega_q t)} + \text{herm. conj.} \tag{6}$$

where G is the number of atoms in the crystal (which is assumed here to be finite) and M their mass. q stands for the phonon wave vector $\boldsymbol{q}$ and the polarisation index $s = 1, 2, 3$, $q = (s, \boldsymbol{q})$. $\boldsymbol{e}_q$ is a polarization vector satisfying

$$(\boldsymbol{e}_{s,\boldsymbol{q}}\, \boldsymbol{e}_{s'\boldsymbol{q}}) = \delta_{ss'}; \qquad \text{all } \boldsymbol{q} \tag{7}$$

b_q is an absorption operator which obeys the commutation rule

$$[b_q,\, b_{q'}^*] = \delta_{qq'} \tag{8}$$

Then the free phonon Hamiltonian is

$$\mathfrak{H}_{Ph} = \frac{M}{2} \sum_{\alpha} (\dot{\boldsymbol{u}}_{\alpha}^2 - \boldsymbol{u}_{\alpha}\, \ddot{\boldsymbol{u}}_{\alpha}) = \sum_{q} n_q\, \omega_q \tag{9}$$

where

$$n_q = b_q^*\, b_q \tag{10}$$

is the number of phonons in state q. In $\mathfrak{H}_{Ph}$ the zero point energy has been eliminated by an appropriate ordering of operators.

For the electron-phonon interaction we take (see e.g. PEIERLS[6]), p. 125)

$$\mathfrak{H}_{int} = \sum_{\alpha} \boldsymbol{W}(\boldsymbol{x} - \boldsymbol{R}_{\alpha})\, \boldsymbol{u}_{\alpha}(0) \tag{11}$$

which in second quantization leads to

$$\left.\begin{aligned} \mathfrak{H}_i = \sum_{k} \sum_{k'} a_k^*(k\,|\,\mathfrak{H}_{int}\,|\,k')\, a_{k'} = \\ = \sum_{k} \sum_{k'} \sum_{q} (k\,|\,C_q\,|\,k')\, a_k^*\, a_{k'}\, b_q + \text{herm. conj.} \end{aligned}\right\} \tag{12}$$

with

$$C_q(\boldsymbol{x}) = (2\,G\,M\,\omega_q)^{-\frac{1}{2}} \sum_{\alpha} \boldsymbol{e}_q\, \boldsymbol{W}(\boldsymbol{x} - \boldsymbol{R}_{\alpha})\, e^{i\,\boldsymbol{q}\,\boldsymbol{R}_{\alpha}} \tag{12'}$$

Our task is now to analyse the canonical ensemble defined by the total Hamiltonian

$$\mathfrak{H}_{total} = \mathfrak{H}_f + \mathfrak{H}_i \tag{13}$$

where

$$\mathfrak{H}_f = \mathfrak{H}_{El} + \mathfrak{H}_{Ph} \tag{13'}$$

is the free Hamiltonian, by treating the electron-phonon interaction $\mathfrak{H}_i$ and later also the magnetic field as perturbations. As usual we circumvent the subsidiary condition that

$$N = \sum_{k} N_k \tag{14}$$

should be constant by going to the grand canonical ensemble where this condition is relaxed by introducing a Lagrange multiplier ζ, the Fermi energy. Then

$$e^{-\alpha\, \Omega_{total}} = \text{Trace}\; e^{-\alpha\,(\mathfrak{H}_{total} - N\,\zeta)}; \quad \alpha \equiv \frac{1}{k\,T} \tag{15}$$

defines the total thermodynamic potential $\Omega_{total} = \varphi_{total} - \bar{N} \cdot \zeta$ and the total free energy φ_{total}, $\bar{N}$ being the average number of electrons.

The perturbation expansion in $\mathfrak{H}_i$ can be performed exactly in the same way as in section 2 of ref. 1, writing

$$e^{-\alpha\, \Omega_{total}} = \frac{1}{2\,\pi\,i} \oint dz\, e^{-\alpha\, z}\, \text{Trace}\; (z - \mathfrak{H}_{total} + N\,\zeta)^{-1} \tag{16}$$

and

$$\left.\begin{aligned}(z-\mathfrak{H}_{total}+N\zeta)^{-1} &= (z-\mathfrak{H}_f+N\zeta)^{-1}+\\ &+(z-\mathfrak{H}_f+N\zeta)^{-1}\mathfrak{H}_i(z-\mathfrak{H}_f+N\zeta)^{-1}+\\ &+(z-\mathfrak{H}_f+N\zeta)^{-1}\mathfrak{H}_i(z-\mathfrak{H}_f+N\zeta)^{-1}\mathfrak{H}_i(z-\mathfrak{H}_f+N\zeta)^{-1}+\cdots\end{aligned}\right\} \quad (16')$$

By going into the representation where the occupation numbers N_k and n_q are diagonal the trace of the first order term in (16′) is seen to vanish since $\mathfrak{H}_f$ is diagonal and $\mathfrak{H}_i$ has no diagonal elements. Therefore we can write

$$\left.\begin{aligned}\Omega_{total} &= \Omega_f+\Omega'+\cdots\\ e^{-\alpha\Omega_{total}} &= e^{-\alpha\Omega_f}(1-\alpha\Omega'+\cdots)\end{aligned}\right\} \quad (17)$$

where

$$e^{-\alpha\Omega_f} = \mathrm{Trace}\, e^{-\alpha(\mathfrak{H}_f-N\zeta)} \quad (17')$$

and

$$\left.\begin{aligned}-\alpha e^{-\alpha\Omega_f}\Omega' = \frac{1}{2\pi i}\oint dz\, e^{-\alpha z}\,\mathrm{Trace}\,[&(z-\mathfrak{H}_f+N\zeta)^{-1}\cdot\\ &\cdot\mathfrak{H}_i(z-\mathfrak{H}_f+N\zeta)^{-1}\mathfrak{H}_i(z-\mathfrak{H}_f+N\zeta)^{-1}]\end{aligned}\right\} \quad (17'')$$

Calling $|A>$ a general state in the representation by the occupation numbers N_k, n_q, N_A the value of (14) and E_A the eigenvalue of $\mathfrak{H}_f$ in this state,

$$\mathfrak{H}_f|A> = E_A|A> \quad (18)$$

eqs. (17′) and (17″) read

$$e^{-\alpha\Omega_f} = \sum_A e^{-\alpha(E_A-N_A\zeta)} \quad (19)$$

and

$$-\alpha e^{-\alpha\Omega_f}\Omega' = \frac{1}{2\pi i}\oint dz\, e^{-\alpha z}\sum_A\sum_B (z-E_A+N_A\zeta)^{-2}\cdot$$

$$\cdot\langle A|\mathfrak{H}_i|B\rangle(z-E_B+N_B\zeta)^{-1}\langle B|\mathfrak{H}_i|A\rangle$$

Making use of (3.18) and of the identity

$$\frac{e^{-\alpha a}-e^{-\alpha b}}{a-b} = -e^{-\alpha b}\int_0^\alpha d\lambda\, e^{-\lambda(a-b)}$$

we obtain

$$\left.\begin{aligned}-\alpha e^{-\alpha\Omega_f}\Omega' = \sum_A\sum_B |\langle A|\mathfrak{H}_i|B\rangle|^2 e^{-\alpha(E_B-N_B\zeta)}\cdot\\ \cdot\int_0^\alpha \lambda\, d\lambda\, e^{-\lambda[E_A-N_A\zeta-(E_B-N_B\zeta)]}\end{aligned}\right\} \quad (20)$$

We first want to calculate the expressions

$$S_{kk'q} \equiv \sum_B \langle A | \mathfrak{H}_i | B \rangle \langle B | a_k^* a_{k'} b_q | A \rangle e^{-\lambda (E_B - N_B \zeta)}$$

$$T_{kk'q} \equiv \sum_B \langle A | \mathfrak{H}_i | B \rangle \langle B | a_{k'}^* a_k b_q^* | A \rangle e^{-\lambda (E_B - N_B \zeta)}$$

for $k \neq k'$. Let

$$|A> = |\ldots, N_k, \ldots, N_{k'}, \ldots, n_q, \ldots> \tag{21}$$

Then there is just one state $|B>$ which contributes to S and T. Since

$$a_k |N_k> = \sqrt{N_k}\,|1 - N_k>; \quad a_k^* |N_k> = \sqrt{1 - N_k}\,|1 - N_k>$$

$$b_q |n_q> = \sqrt{n_q}\,|n_q - 1>; \quad b_q^* |n_q> = \sqrt{n_q + 1}\,|n_q + 1>$$

it follows from (12) and (3), (9) that

$$S_{kk'q} = (k|C_q|k')^* (1 - N_k) N_{k'} n_q e^{-\lambda (E_A - N_A \zeta + W_k - W_{k'} - \omega_q)}$$

$$T_{kk'q} = (k|C_q|k') N_k (1 - N_{k'}) (n_q + 1) e^{-\lambda (E_A - N_A \zeta - W_k + W_{k'} + \omega_q)}$$

The case $k = k'$ need not be considered since from gauge invariance it follows that $(k \mid C_q \mid k) = 0$ for $\boldsymbol{q} \neq 0$. Indeed, a shift of the coordinate system through $\boldsymbol{R}_\alpha$ induces a gauge transformation

$$\boldsymbol{A}(\boldsymbol{x} - \boldsymbol{R}_\alpha) = \boldsymbol{A}(\boldsymbol{x}) + \frac{\partial \Lambda}{\partial \boldsymbol{x}}; \quad \psi(\boldsymbol{x} - \boldsymbol{R}_\alpha) = e^{i e \Lambda(\boldsymbol{x})} \psi(\boldsymbol{x})$$

with

$$\Lambda(\boldsymbol{x}) = \tfrac{1}{2} \boldsymbol{H} (\boldsymbol{x} \times \boldsymbol{R}_\alpha)$$

$\boldsymbol{A}(x)$ being given by (2.8). Therefore

$$\psi^* (\boldsymbol{x} - \boldsymbol{R}_\alpha) \boldsymbol{W} (\boldsymbol{x} - \boldsymbol{R}_\alpha) \psi (\boldsymbol{x} - \boldsymbol{R}_\alpha) = \psi^*(\boldsymbol{x}) \boldsymbol{W} (\boldsymbol{x} - \boldsymbol{R}_\alpha) \psi(\boldsymbol{x})$$

Integrating over the crystal volume (which here again is assumed to be infinite) it follows that

$$\int d^3 x\, \psi^*(\boldsymbol{x}) \sum_\alpha \boldsymbol{W}(\boldsymbol{x} - \boldsymbol{R}_\alpha) e^{i \boldsymbol{q} \boldsymbol{R}_\alpha} \psi(\boldsymbol{x}) = \sum_\alpha e^{i \boldsymbol{q} \boldsymbol{R}_\alpha} \int d^3 x\, \psi^*(\boldsymbol{x}) \boldsymbol{W}(\boldsymbol{x}) \psi(\boldsymbol{x})$$

which for $\boldsymbol{q} \neq 0$ is zero on account of (A. 4). Thus

$$\left.\begin{aligned} &\sum_B |\langle A | \mathfrak{H}_i | B \rangle|^2 e^{-\lambda (E_B - N_B \zeta)} = e^{-\lambda (E_A - N_A \zeta)} \sum_k \sum_{k'} \sum_q |(k|C_q|k')|^2 \\ &\{(1 - N_k) N_{k'} n_q e^{-\lambda (W_k - W_{k'} - \omega_q)} + N_k (1 - N_{k'}) (n_q + 1) e^{+\lambda (W_k - W_{k'} - \omega_q)}\} \end{aligned}\right\} \tag{22}$$

Since according to (21)

$$E_A = \sum_k N_k W_k + \sum_q n_q \omega_q \tag{23}$$

we have from (19), (14)

$$\left.\begin{aligned} e^{-\alpha \Omega_f} &= \prod_k \left(\sum_{N_k = 0,1} e^{-\alpha (W_k - \zeta) N_k} \right) \prod_q \left(\sum_{n_q = 0}^{\infty} e^{-\alpha \omega_q n_q} \right) = \\ &= \prod_k (1 + e^{-\alpha (W_k - \zeta)}) \prod_q (1 - e^{-\alpha \omega_q})^{-1} \end{aligned}\right\} \tag{24}$$

or $$\Omega_f = -\frac{1}{\alpha}\sum_k \log\left(1 + e^{-\alpha(W_k-\zeta)}\right) + \frac{1}{\alpha}\sum_q \log\left(1 - e^{-\alpha\omega_q}\right) \quad (24')$$

Here the electron part (note that spin is neglected in (2)) is identical with $V/2\cdot\Omega$ as defined in (2.2, 4). With the help of eqs. (22), (23), (24), (19), eq. (20) can be written as

$$-\alpha\Omega' = \sum_k \sum_{k'} \sum_q |(k|C_q|k')|^2 \sum_{N_k=0,1} \sum_{N_{k'}=0,1} \sum_{n_q=0}^{\infty} \Bigg\{ (1-N_k)\cdot N_{k'}\, n_q \int_0^\alpha \lambda\, d\lambda\, e^{-\lambda(W_k - W_{k'} - \omega_q)} + N_k(1-N_{k'})(n_q+1)\cdot \int_0^\alpha \lambda\, d\lambda\, e^{+\lambda(W_k - W_{k'} - \omega_q)} \Bigg\} \Bigg[\sum_{N_k=0,1} e^{-\alpha(W_k-\zeta)N_k} \cdot \sum_{N_{k'}=0,1} e^{-\alpha(W_{k'}-\zeta)N_{k'}} \sum_{n_q=0}^{\infty} e^{-\alpha\omega_q n_q} \Bigg]^{-1}$$

Introducing average occupation numbers

$$\bar{N}_k \equiv \sum_{N_k=0,1} N_k e^{-\alpha(W_k-\zeta)N_k} \Bigg[\sum_{N_k=0,1} e^{-\alpha(W_k-\zeta)N_k}\Bigg]^{-1} = (e^{\alpha(W_k-\zeta)}+1)^{-1} \equiv f(W_k) \quad (25)$$

$$\bar{n}_q \equiv \sum_{n_q=0}^{\infty} n_q\, e^{-\alpha\omega_q n_q} \Bigg[\sum_{n_q=0}^{\infty} e^{-\alpha\omega_q n_q}\Bigg]^{-1} = (e^{\alpha\omega_q}-1)^{-1} \equiv g(\omega_q) \quad (26)$$

(note that in (25) f is the Fermi function introduced in (4.1)) the last expression for $-\alpha\Omega'$ becomes

$$-\alpha\Omega' = \sum_k \sum_{k'} \sum_q |(k|C_q|k')|^2 \cdot \Bigg\{ (1-\bar{N}_n)\,\bar{N}_{k'}\,\bar{n}_q \int_0^\alpha \lambda\, d\lambda\, e^{-\lambda(W_k - W_{k'} - \omega_q)} + \bar{N}_k(1-\bar{N}_{k'})(\bar{n}_q+1) \int_0^\alpha \lambda\, d\lambda\, e^{+\lambda(W_k - W_{k'} - \omega_q)} \Bigg\} \quad (27)$$

This formula may be simplified further by exploiting the symmetry of C_q which in view of the relations

$$\omega_{\tilde{q}} = \omega_q;\ \boldsymbol{e}_{\tilde{q}} = \boldsymbol{e}_q;\ q \equiv (s, \boldsymbol{q});\ \tilde{q} \equiv (s, -\boldsymbol{q})$$

and of its definition (12′) is

$$C_q^* = C_{\tilde{q}}$$

Thus

$$|(k|C_q|k')|^2 = |(k'|C_{\tilde{q}}|k)|^2$$

and after relabelling the summation indices in the second term of the curled bracket of (27) according to $k \to k'$, $k' \to k$, $q \to \tilde{q}$ this formula simplifies to

$$\left.\begin{aligned} -\alpha\,\Omega' = \sum_k \sum_{k'} \sum_q |(k|C_q|k')|^2 (1-\bar{N}_k)\bar{N}_{k'} \cdot \\ \cdot \int_0^\alpha \lambda\, d\lambda\, e^{-\lambda(W_k - W_{k'})} \{\bar{n}_q\, e^{+\lambda\omega_q} + (\bar{n}_q+1)\, e^{-\lambda\omega_q}\} \end{aligned}\right\} \quad (28)$$

For the evaluation of Ω' as a perturbation expansion in the magnetic field it is important that eq. (28) may be rewritten in a form which is independent of the representation (2). In fact, with use of (25), (26) we can write

$$\left.\begin{aligned} -\alpha\,\Omega' = \sum_q \int_0^\alpha \lambda\, d\lambda\, \mathrm{Trace}\,[(1-f(\mathfrak{H}))\, e^{-\lambda\mathfrak{H}} \cdot \\ \cdot C_q\, f(\mathfrak{H})\, e^{+\lambda\mathfrak{H}}\, C_q^*]\, g(\omega_q)\, (e^{+\lambda\omega_q} + e^{(\alpha-\lambda)\omega_q}) \end{aligned}\right\} \quad (28')$$

where now the trace goes over one-electron states as in (2.2). The modification of the electronic thermodynamic potential Ω, eqs. (2.1, 2), due to the interaction with the phonons is

$$\frac{2}{v}\,\Omega' = \Omega_{int}^{(0)} - \frac{1}{2}\,\chi_{int}\,H^2 + \cdots \quad (29)$$

where χ_{int} is the additional susceptibility due to this interaction. The calculation of Ω' as a power series in the magnetic field H can, in principle, be carried through with the method used in ref. 1, writing the functions $(1-f(\mathfrak{H}))\cdot\exp(-\lambda\mathfrak{H})$ and $f(\mathfrak{H})\cdot\exp(+\lambda\mathfrak{H})$ in (28') as Cauchy integrals and making use of the expansion (2.6). The evaluation may again be carried out in the field free representation (2.7).

The matrix element of C_q in this representation is obtained by means of a reduction of the domain of integration to the cell Ω_0 using (A. 1, 2),

$$\begin{aligned}(2\,G\,M\,\omega_q)^{\frac{1}{2}}\,(n\,\boldsymbol{k}|C_q|n'\,\boldsymbol{k}') &= \sum_\alpha e^{i\,\boldsymbol{q}\,\boldsymbol{R}_\alpha}\,\boldsymbol{e}_q\,(n\,\boldsymbol{k}|\,\boldsymbol{W}(\boldsymbol{x}-\boldsymbol{R}_\alpha)\,|n'\,\boldsymbol{k}') \\ &= \sum_\alpha \sum_\beta e^{i\,\boldsymbol{q}\,\boldsymbol{R}_\alpha}\, e^{i(\boldsymbol{k}'-\boldsymbol{k})\,\boldsymbol{R}_\beta} \int_{\Omega_0} d^3x'\, u_{n\,\boldsymbol{k}}^*(\boldsymbol{x}') \\ &\quad \cdot u_{n'\,\boldsymbol{k}'}(\boldsymbol{x}')\, e^{i(\boldsymbol{k}'-\boldsymbol{k})\,x'}\,\boldsymbol{e}_q\,\boldsymbol{W}(\boldsymbol{x}'+\boldsymbol{R}_\beta-\boldsymbol{R}_\alpha).\end{aligned}$$

With

$$\boldsymbol{R}_\beta - \boldsymbol{R}_\alpha = \boldsymbol{R}_\gamma$$

this may be written as

$$\begin{aligned}(2\,G\,M\,\omega_q)^{\frac{1}{2}}\,(n\,\boldsymbol{k}|C_q|n'\,\boldsymbol{k}') &= \sum_\alpha e^{i(\boldsymbol{q}+\boldsymbol{k}'-\boldsymbol{k})\,\boldsymbol{R}_\alpha} \\ &\quad \cdot \sum_\gamma \int_{\Omega_0} d^3x'\, e^{i(\boldsymbol{k}'-\boldsymbol{k})(\boldsymbol{x}'+\boldsymbol{R}_\gamma)}\, u_{n\,\boldsymbol{k}}^*\, u_{n'\boldsymbol{k}'}\,\boldsymbol{e}_q\,\boldsymbol{W}(\boldsymbol{x}'+\boldsymbol{R}_\gamma)\end{aligned}$$

Making use of (A.4) and going back to the full domain of integration we obtain

$$(n\,\boldsymbol{k}\,|\,C_q\,|\,n'\,\boldsymbol{k}') = \frac{(2\pi)^3}{v}\,\delta(\boldsymbol{q}+\boldsymbol{k}'-\boldsymbol{k})\;(2\,G\,M\,\omega_q)^{-\frac{1}{2}}\;\boldsymbol{e}_q(n\,\boldsymbol{k}\,|\,\boldsymbol{W}(\boldsymbol{x})\,|\,n'\,\boldsymbol{k}') \tag{30}$$

3. Temperatur dependence of Ω'

It is evident from eq. (28') that, due to the phonon variables but also to the λ-integration, a new type of temperature variation is present in Ω'. With the use of (30) we may write eq. (28') as

$$\Omega' = -\frac{1}{\alpha}\int_0^{\alpha}\lambda\,d\lambda\sum_{s=1}^{3}\int d^3q\,\frac{e^{\lambda\omega_q}+e^{(\alpha-\lambda)\omega_q}}{e^{\alpha\omega_q}-1}\cdot\frac{e_{qj}\,e_{qj'}}{\omega_q}\,T_{jj'}(\alpha,\lambda,\boldsymbol{q})$$

where e_{qj} is the j-component of the polarisation vector $\boldsymbol{e}_q$. To simplify the discussion we assume that

$$\omega_{s,\,\boldsymbol{q}} = c_s\,|\boldsymbol{q}|$$

c_s being the velocity of phonons of mode $s = 1, 2, 3$. With the new variables

$$x \equiv \alpha\,\omega_q; \qquad \xi \equiv \frac{\lambda}{\alpha}; \qquad x_m = \alpha\,\omega_m \cong \frac{\Theta}{T}$$

where ω_m is the maximum frequency and Θ the Debye temperature, we obtain

$$\Omega' = -\frac{1}{\alpha}\int_0^1\xi\,d\xi\left(\sum_{s=1}^{3}c_s^{-3}\right)\int_0^{x_m}x\,dx\,\frac{e^{\xi x}+e^{(1-\xi)x}}{e^x-1}\oint d\Omega_q\,e_{qj}\,e_{qj'}\,T_{jj'}$$

In the temperature region of interest, $\Theta \gg T$ holds, so that we can replace the limit of integration x_m by infinity. Now in tight binding approximation T_{jj}, does not depend on $\boldsymbol{q}$ as is seen from (30), (28) and Appendix C of ref. 1, so that, recalling (7),

$$\Omega' = -\frac{1}{\alpha}\cdot\frac{4\pi}{3}\sum_{s=1}^{3}c_s^{-3}\int_0^1\xi\,d\xi\sum_{j=1}^{3}T_{jj}(\alpha,\xi\alpha)\int_0^{\infty}x\,dx\,\frac{e^{\xi x}+e^{(1-\xi)x}}{e^x-1}$$

Thus Ω' contains an overall factor $1/\alpha = kT$ in addition to the dependence of T_{jj} on α. According to (29) the same is true for χ_{int}, so that

$$\chi_{total} = \chi + \chi_{int} \tag{31}$$

is likely to account for the behaviour (1).

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