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Structural origin of magnetic birefringence in rutile-type antiferromagnets

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The microscopic origin of magnetic birefringence in the rutile-type antiferromagnets XF_2 (X=Mn, Fe, Co, or Ni) is analyzed on the basis of the theory of structural birefringence developed by Ewald and Born. The general principles of the Ewald-Born theory are reviewed. The magnetic birefringence can be explained by a small exchange-induced internal displacement of the fluorine atoms. Predictions from theory are compared with accurate crystal-structure analyses based on γ-ray-diffraction data. The agreement found between theory and experiment is excellent.

I. INTRODUCTION

The temperature dependence of the optical linear birefringence (Δn) from magnetically ordered, transparent crystals has been the subject of a large number of studies during the past 20 years (see review[1]). In spite of the absence of a net magnetization in antiferromagnets, Δn varies strongly near the Néel temperature and a magnetic contribution occurs which is superimposed onto the temperature-dependent natural birefringence of an optically anisotropic crystal.

There has been some controversy about the microscopic origin of the magnetic birefringence (e.g., Ref. 1), whether the dominant contribution is (i) of purely electronic origin (modification of the electron transitions caused by the exchange field) or due to (ii) magnetostrictive distortions of the crystal structure [any change of the unit cell (bulk magnetostriction) as well as relative shifts of the atomic positions (internal displacements) within the unit cell].

The antiferromagnetic rutile-type transition-metal difluorides XF_2 (X=Mn, Fe, Co, or Ni) were among the first compounds to be investigated in detail,[2-6] and a proportionality between the magnetic birefringence and the magnetic internal energy has been established. Rutile-type structures are determined by the two lattice constants a and c and a parameter x, which specifies the position of the fluorine atoms along the diagonal [110]. Information about the microscopic origins of this birefringence was tried to obtain from (i) the variation of Δn with the observed macroscopic strain and (ii) under applied uniaxial stress. From a comparison of the temperature derivative of Δn with the temperature dependence of the anisotropy in the lattice expansion, Jahn[3] found that the observed Δn could not be explained by lattice parameter changes alone and concluded Δn to be strongly dependent on an internal distortion. For the case of NiF_2 this distortion has been attributed[7] to a small change of the positional parameter x. Borovik-Romanov, Kreĭnes, and Pačes[8] have studied the birefringence of MnF_2 under applied stress. They found that a stress along [110] resulted only in a small change in Δn and concluded that "there is no support that the fluorine parameter has a significant influence on the birefringence."

In the present work the microscopic origin of the magnetic birefringence of the difluorides is reexamined from both a theoretical and an experimental point of view. The paper is organized as follows. In Sec. II and in the Appendix, the Ewald-Born theory of birefringence is briefly outlined. Despite the fact that this theory is quite old, it is not very well known and no concise description has been found in the recent literature. The wave propagation in the crystal is treated in a consistently microscopic manner. Although the final equations remain unchanged, this approach differs from the elementary theory of polarization where the crystal is subjected to an external field and retardation is neglected. In Sec. III the Ewald-Born theory is used to examine the magnetic birefringence in terms of crystal-structure deformations. In Sec. IV predicted values of distortions are tested by comparison with results obtained from accurate γ-ray-diffraction experiments.

II. THEORY OF BIREFRINGENCE

The microscopic theory of crystal optics as developed by Ewald[9] and Born[10] is based on the model of harmonically oscillating dipoles arranged in an infinitely large crystal lattice. According to the Ewald-Born theory, a plane electromagnetic wave should exist self-consistently in the crystal. This means that the spherical waves emitted with velocity c from the dipoles should add up to a plane wave traveling with velocity v. The vibration of each dipole is just maintained by the field produced by all the other dipoles (no incident beam). The refractive index $n=c/v$ follows from the condition of self-consistency. In a noncubic arrangement the force acting on a dipole is different for different directions of the field, thus giving rise to birefringence.

The position vector of an atom k with respect to an arbitrary origin will be denoted by $\mathbf{x}(lk)=\mathbf{x}(l)+\mathbf{x}(k)$, where $\mathbf{x}(l)=l_1\mathbf{a}_1+l_2\mathbf{a}_2+l_3\mathbf{a}_3$ is the lattice vector, $\mathbf{a}_1,\mathbf{a}_2,\mathbf{a}_3$ being the basic vectors of the unit cell, and $\mathbf{x}(k)$ is the base vector within the cell. The cell contains s atoms, and so $k=1,\dots,s$. An interatomic vector is denoted by $\mathbf{x}(lk,k')=\mathbf{x}(lk)-\mathbf{x}(k')$.

It will be assumed that for each atom k the electric dipole moment $\mathbf{p}(k)$ induced under the influence of an electromagnetic field is proportional to the field $\mathbf{E}(k)$ acting at its center,

$$\mathbf{p}(k)=\alpha(k)\mathbf{E}(k)\;, \tag{1}$$

where $\alpha(k)$ is the (isotropic) electronic polarizability of atom k. In a dipole lattice, $\mathbf{E}(k)$ is the electric field due to all dipoles except $\mathbf{p}(k)$ (exciting field). In computing $\mathbf{E}(k)$ one has to take into account that the field of each dipole $\mathbf{p}(l'k')$ will arrive at $\mathbf{x}(k)$ at a different time $(1/c)x(l'k',k)$, i.e., the effect of retardation.

The exciting field can be separated into the macroscopic field $\bar{\mathbf{E}}$ and an inner field:

$$\mathbf{E}(k)=\bar{\mathbf{E}}+\sum_{k'}\mathsf{Q}(kk')\mathbf{p}(k')\;, \tag{2}$$

where the coefficients $\mathsf{Q}(kk')$ form tensors of second rank (local-field tensors), which only depend on the crystal structure (see Appendix). Substitution of (2) into (1) leads to a linear system of equations for the components $p_\alpha(k)$:

$$\sum_{\beta}\sum_{k'}\left[\frac{1}{\alpha(k)}\delta_{\alpha\beta}\delta_{kk'}-Q_{\alpha\beta}(kk')\right]p_\beta(k')=\bar{E}_\alpha\;. \tag{3}$$

Introducing the symmetric matrix R inverse to the $3s\times 3s$ matrix,

$$R^{-1}_{\alpha\beta}(kk')=\frac{1}{\alpha(k)}\delta_{\alpha\beta}\delta_{kk'}-Q_{\alpha\beta}(kk')\;,$$

the system (3) has the solution

$$p_\alpha(k)=\sum_{\beta}\sum_{k'}R_{\alpha\beta}(kk')\bar{E}_\beta\;, \tag{4}$$

and the polarization per unit volume is given by

$$P_\alpha=\frac{1}{V}\sum_{k}p_\alpha(k)=\frac{1}{V}\sum_{\beta}\sum_{k,k'}R_{\alpha\beta}(kk')\bar{E}_\beta\;, \tag{5}$$

where V is the unit-cell volume. The components of the dielectric displacement vector, which is defined by $\bar{\mathbf{D}}=\bar{\mathbf{E}}+4\pi\mathbf{P}$, can therefore be written as

$$\bar{D}_\alpha=\bar{E}_\alpha+\frac{4\pi}{V}\sum_{\beta}\sum_{k,k'}R_{\alpha\beta}(kk')\bar{E}_\beta\;, \tag{6}$$

which has the same form as the phenomenological relation

$$\bar{D}_\alpha=\sum_{\beta}\epsilon_{\alpha\beta}\bar{E}_\beta\;. \tag{7}$$

Thus the dielectric tensor is given by

$$\epsilon_{\alpha\beta}=\delta_{\alpha\beta}+\frac{4\pi}{V}\sum_{k,k'}R_{\alpha\beta}(kk')\;. \tag{8}$$

Equation (8) connects the dielectric tensor with the polarizabilities and the crystal structure. With Maxwell's relation $\epsilon=n^2$, the optical birefringence is expressed as

$$\Delta n_{\alpha\beta}=\sqrt{\epsilon_{\alpha\alpha}}-\sqrt{\epsilon_{\beta\beta}}\;.$$

The dispersion of the refractive indices is implicitly contained in the polarizability, which is a function of frequency.

III. APPLICATION TO RUTILE-TYPE DIFLUORIDES

The transition-metal difluorides $X\mathrm{F}_2$ (X=Mn, Fe, Co, Ni, or Zn) have the tetragonal rutile-type structure (space group $P4_2/mnm$). The cations are located at the positions $0,0,0$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ and the anions are at $\pm(x,x,0;\frac{1}{2}-x,\frac{1}{2}+x,\frac{1}{2})$.

The local-field tensors $\mathsf{Q}(kk')$ for room temperature were evaluated using the structural data given in Table I. It should be noted that the structure data are fairly accurate except for the fluorine positional parameter x of $\mathrm{CoF_2}$ and $\mathrm{ZnF_2}$.

Convergence of the lattice sums has always been checked using the relation for the invariance of the trace $(V/4\pi)\sum_\alpha Q_{\alpha\alpha}(kk')=1$. Independent calculation of the xx and zz components resulted in deviations from 1 of the order of 10^{-14} with the summation over a few hundred unit cells. Accuracy of the calculations is of crucial importance since small differences in the calculated values of $Q_{\alpha\beta}(kk')$ may result in rather large differences in the calculated birefringence. An iterative improvement of the solution to the linear equation system (4) has been applied. The crystal symmetry leads to a twofold simplification of the computations: (i) relations are im-

TABLE I. Crystal data and refractive indices (λ=6328 Å) at room temperature.

	$\mathrm{MnF_2}$	$\mathrm{FeF_2}$	$\mathrm{CoF_2}$	$\mathrm{NiF_2}$	$\mathrm{ZnF_2}$	$\mathrm{MgF_2}$
a (Å)[a]	4.8736	4.6974	4.6950	4.6501	4.7037	4.6213[b]
c (Å)[a]	3.3101	3.3082	3.1785	3.0835	3.1334	3.0519[b]
x	0.3049[c]	0.3013[d]	0.303[a]	0.3037[e]	0.305[a]	0.3029[b]
n_e [f]	1.4992	1.5213	1.5331	1.5562	1.5229	1.3779
n_o [f]	1.4706	1.5113	1.5069	1.5212	1.4937	1.3664

[a] Reference 11.
[b] Reference 12.
[c] Reference 13.
[d] Reference 14.
[e] Reference 15.
[f] Reference 3.

TABLE II. Anion and cation polarizabilities (in units of Å^3) at room temperature ($\lambda = 6328$ Å).

	Mn	Fe	Co	Ni	Zn	Mg
α(cation)	1.1138	1.3327	1.1883	1.1418	0.8453	0.4638
$\alpha(F)$	0.7268	0.5821	0.6095	0.6041	0.7601	0.6358

posed on the various components of $Q(kk')$, and (ii) only linear combinations of dipole moments which transform according to a particular irreducible representation of the space group have to be considered. Detailed descriptions of these aspects are to be found in Refs. 16–18 which deal with the rutile structure.

Table II shows the set of polarizabilities that reproduce the refractive indices at room temperature for $\lambda = 6328$ Å. It was deduced from (8) by a trial-and-error variation of $\alpha(F)$ within physically reasonable limits. For each value of $\alpha(F)$, the corresponding value of α(cation) was determined from the equation for n_e. This procedure was repeated until agreement was obtained between the observed and calculated values of n_o.

In the calculation of the birefringence at low temperature, the following two steps were adopted. The polarizabilities were always held fixed at the values derived for room temperature (Table II). In the first step only the influence of the changes in the lattice constants with temperature were taken into consideration. The low-temperature lattice constants were taken from Haefner[11] and are given in Table III. The very small orthorhombic distortion in NiF_2 has been neglected. The values of the birefringence thus calculated are given in Table IV. As can be seen clearly, no agreement is obtained with the observed birefringence of the antiferromagnetic compounds. The calculated effect of spontaneous striction results in an increase of the birefringence as the temperature is lowered, which is opposite to the observations.

The birefringence is extremely sensitive to the fluorine position, and in the second step the positional parameter x was allowed to vary in such a way that the observed birefringence was reproduced. The sensitivity of Δn with respect to x has already been noted by Hylleraas[16] in rutile, and he actually proposed to improve the results obtained from x-ray diffraction by optical calculations.

As to be expected, the changes in the lattice constants alone do not account for the magnetic birefringence; rather, one has to assume a small shift of the fluorine atoms (see Table V). This shift has to be considered as a result of the exchange interaction between the cation spins which is transmitted through the intervening fluorine atoms, and indeed a negligible shift is obtained for the diamagnets ZnF_2 and MgF_2. Table VI shows the temperature variation of the atomic shift in MnF_2 as calculated from Δn_{obs}. Both the short- and long-range magnetic order contribute to the birefringence. The onset of short-range order at $(2.5-3)T_N$ is clearly reflected by the calculated shift.

IV. COMPARISON WITH EXPERIMENT

The suggested temperature variation of the fluorine positional parameter may be tested by means of x-ray-diffraction analysis. Since the calculated atomic shifts are very small, one has to refer to Bragg diffraction data of very high precision. It has been demonstrated that single-crystal diffraction of γ rays emitted from a radioactive source such as ^{198}Au or ^{192}Ir leads to structure factors of higher accuracy as compared to x-ray diffraction.[20] Some sources of systematic error which limit the accuracy of structure factors derived from x-ray-diffraction data are absent for γ rays. The reason behind that lies in the much shorter wavelengths of the γ rays, resulting in a much weaker interaction with matter (basic condition for the validity of the first Born approximation) and in the intrinsically highly monochromatized beam. γ-ray-diffraction measurements from both MnF_2 and NiF_2 have provided the experimental basis against which the predicted atomic shifts have been tested.

A. MnF_2

Selected γ-ray-diffraction data ($\lambda = 0.0301$ Å) collected from a single-crystal plate gave $\Delta x = x(295\text{ K}) - x(15\text{ K}) = 48(8.6)\times 10^{-5}$, where the number in parentheses refers to one standard deviation.[21] Refinement of complete γ-ray data sets ($\lambda = 0.0392$ Å) collected from a single-crystal sphere resulted in $\Delta x = 49(11.3)\times 10^{-5}$.[13] The weighted mean value of the two independent experiments is $\Delta x = 48.4(6.8)\times 10^{-5}$, which is in excellent agreement with the calculated value.

Accurate neutron-diffraction studies[22] revealed a difference of 1.5×10^{-3} Å in the fluorine position at 15 K

TABLE III. Lattice constants at low temperature.

	MnF_2	FeF_2	CoF_2	NiF_2	ZnF_2	MgF_2
T (K)	4	15	15	21	48	20
a (Å)[a]	4.8736	4.6933	4.6941	4.6478[b]	4.6997	4.6167[c]
c (Å)[a]	3.2998	3.3007	3.1698	3.0745	3.1277	3.0458[c]

[a] Reference 11.

[b] Mean value of the orthorhombic lattice constants.

[c] Derived from the thermal expansion coefficients (Ref. 19).

TABLE IV. Observed and calculated birefringence ($\times 10^4$), $\Delta n = n_e - n_o$, at low temperature.

	MnF_2	FeF_2	CoF_2	NiF_2	ZnF_2	MgF_2
T (K)	10	13	14	20	40	20
Δn_{obs} [a]	273.73	91.92	263.99	334.19	294.54	116.42
Δn_{calc} [b]	293.38	102.79	268.90	357.71	295.35	116.55
Δn_{calc} [c]	273.74	91.91	263.97	334.19	294.55	116.42
x_{calc}	0.304 404	0.301 071	0.302 897	0.303 246	0.304 980	0.302 892

[a] Reference 3.
[b] $x = x$ (Table I).
[c] $x = x_{\text{calc}}$.

with respect to the position based on the γ-ray data. Whereas γ rays as electromagnetic radiation interact with the electron charge distribution, the neutrons are scattered mainly by interaction with the nuclei. The magnetiostrictive shift of the nuclei amounts to $\Delta x = 28(3) \times 10^{-5}$. The noncoincidence of the centroid of the charge distribution with the nuclear position, however, is not due to valence-shell scattering. The results of charge-density analyses[23] show that it rather reflects a polarization of the fluorine core electrons which is absent in the paramagnetic state. Since the polarizability is determined by the outer electrons, it is the position of the centroid of the charge distribution as determined by γ-ray diffraction which enters in the Ewald-Born theory.

B. NiF_2

NiF_2 is a weak ferromagnet, and therefore the symmetry lowers from tetragonal to orthorhombic at the phase transition. The difference between the lattice constants a and b is very small, amounting to about 10^{-3} Å at 20 K.[24] In the absence of a magnetic field, the crystal divides into domains with the weak ferromagnetic moment in the $\pm a$ or $\pm b$ directions. With a random domain distribution, a diffraction measurement in zero field should provide an averaged structure of tetragonal symmetry. It turned out, however, that the γ-ray-diffraction measurements were rather sensitive with respect to the domain formation. Diffraction data at 15 K have therefore been recollected from a single-domain crystal in a sufficiently strong magnetic field. Refinement of the extensive γ-ray data sets resulted in $\Delta x = 41(7.9) \times 10^{-5}$,[15] which again is in excellent agreement with the calculated value.

V. DISCUSSION

It should be noted that the magnetic birefringence could be explained entirely by the arrangement of the ions, assuming each ion itself to be isotropic. In particular, no change in the polarizability of the magnetic ions had to be assumed.

The negative sign of the magnetic birefringence with respect to the natural birefringence is correlated with the sign of Δx, i.e., with a shortening of the nearest-neighbor distances (CoF_2 is an exception).

Markovin and Pisarev[25] investigated the temperature variation of the principal values of the refractive indices in MnF_2. The slopes $dn_{o,e}(T)/dT$ are found to be positive well above T_N and negative in the magnetically ordered region. Changes in lattice geometry fail to describe these observations; rather, one has to allow for changes in polarizability. Obviously, the birefringence may arise from completely different contributions than the refractive indices. Contributions that affect n_o and n_e in the same manner do not influence the birefringence. The average refractive index of MnF_2, for example, when evaluated from the Lorentz-Lorenz relation, is 1.459, which is quite close to the actual value. Hence deviations from cubic symmetry which govern the birefringence are relatively unimportant for the refractivity.

dn/dT can be separated into three components as arising from (i) the change in the number of polarizable particles per unit volume, (ii) the change in polarizability caused by lattice contraction, and (iii) the pure temperature effect on the polarizability. If (i) were the only mechanism to be operative, it would tend to make dn/dT negative. It is now recognized that the electrostatic crystal potential decreases the effective size of the anions, whereas the corresponding expansion of the cation is much less pronounced.[26,27] Increasing the Madelung potential at an anion site with lattice contraction will result in a decrease of anion polarizability arising from ion compression. Component (ii) will therefore tend to make dn/dT positive. As yet, there is no method of calculating (iii). Hence the temperature coefficient of the refractive index results from a delicate balance between at least two competing factors, and the Ewald-Born theory could account for it only in combination with a sophisticated theory describing the influence of crystal potential and temperature on the polarizability.

Even for the relatively simple rutile-type structures, it was difficult to determine the microscopic origin of the magnetic birefringence. For compounds with more than

TABLE V. Calculated shifts of the F positional parameter $\Delta x_{\text{calc}} = x(\text{room temperature}) - x_{\text{calc}}(\text{low temperature})$.

	MnF_2	FeF_2	CoF_2	NiF_2	ZnF_2	MgF_2
$10^5 \Delta x_{\text{calc}}$	49.6	22.9	10.3	45.4	2.0	0.8

TABLE VI. Temperature variation of the calculated shift Δx_{calc} in MnF_2 ($T_N=67.7$ K).

T (K)	200	100	70	60	50	30	10
$10^5\Delta x_{\text{calc}}$	2.4	6.4	13.4	25.0	33.7	44.9	49.6

one structural degree of freedom, it seems to be impossible to relate changes in the optical anisotropy unambiguously to internal atomic displacements. The rhombohedral antiferromagnets such as MnCO_3 might provide a further opportunity for a quantitative test of the internal displacement mechanism (influence of the oxygen position).

VI. CONCLUSION

The magnetic birefringence in rutile-type antiferromagnets is due to internal atomic displacements. Predicted shifts as small as 3×10^{-3} Å have been confirmed by crystal-structure analyses. From the results obtained above, one can conclude that the classical point-dipole model, upon which the Ewald-Born theory is based, is considerably more powerful than is commonly assumed.

APPENDIX: BASIC ELEMENTS OF THE EWALD-BORN THEORY

Plane-wave representation of the total electric field

The field of dipoles all of which are oscillating in the same direction is most conveniently expressed in terms of the Hertz vector **Z**, which for a single dipole of moment $\mathbf{p}\exp(-i\omega t)$ is defined as

$$\mathbf{Z}(x)=\frac{\mathbf{p}\exp[-i\omega(t-x/c)]}{x}\ , \tag{A1}$$

where x is the distance from the field point to the dipole. The electric field is calculated from the relation

$$\mathbf{E}=\nabla\nabla\cdot\mathbf{Z}-\Delta\mathbf{Z}=\nabla\times\nabla\times\mathbf{Z}\ . \tag{A2}$$

If the phases of the dipoles vary according to a plane wave of wave vector **K**, the amplitude of the Hertz vector at a point **x** is

$$\mathbf{Z}(\mathbf{x})=\sum_{l,k}\mathbf{p}(k)\frac{\exp[iK_0\cdot|\mathbf{x}-\mathbf{x}(lk)|]}{|\mathbf{x}-\mathbf{x}(lk)|}\times\exp[i\mathbf{K}\cdot\mathbf{x}(lk)]\ , \tag{A3}$$

where $K_0=\omega/c$ and $\sum_l$ denotes the sum over all lattice vectors in crystal space. This equation may be recast as

$$\mathbf{Z}(\mathbf{x})=\sum_k\mathbf{p}(k)\exp[i\mathbf{K}\cdot\mathbf{x}(k)]\times\sum_l\frac{\exp[iK_0\cdot|\mathbf{x}-\mathbf{x}(lk)|]}{|\mathbf{x}-\mathbf{x}(lk)|}\times\exp[i\mathbf{K}\cdot\mathbf{x}(l)]\ . \tag{A4}$$

The lattice sum, which consists of a periodic part and a phase shifting factor, may be expanded into a Fourier series, and the Hertz vector is then transformed into a sum of plane waves:

$$\mathbf{Z}(\mathbf{x})=\frac{4\pi}{V}\sum_k\mathbf{p}(k)\exp[i\mathbf{K}\cdot\mathbf{x}(k)]\times\sum_h\frac{\exp\{i[\mathbf{y}(h)+\mathbf{K}]\cdot[\mathbf{x}-\mathbf{x}(k)]\}}{|\mathbf{y}(h)+\mathbf{K}|^2-K_0^2}\ , \tag{A5}$$

with the reciprocal lattice points defined as $\mathbf{y}(h)=2\pi(h_1\mathbf{b}_1+h_2\mathbf{b}_2+h_3\mathbf{b}_3)$ and $\mathbf{a}_i\cdot\mathbf{b}_j=\delta_{ij}$.

Spatial average of the total field

In the visible region of the electromagnetic spectrum, K_0 and K are much smaller than $y(h)$. Hence the leading term in **Z** is the constant term of the Fourier series, $h=0$. It is a plane wave with wave vector **K** corresponding to the mean field obtained by averaging over a region which is large compared with characteristic interatomic distances. It represents the macroscopic field that occurs in Maxwell's equations. With the polarization defined as dipole moment density $\mathbf{P}=\sum_{k'}\mathbf{p}(k')/V$ and $K=2\pi/\lambda$, $K_0=2\pi/\lambda_0$, and $n=\lambda_0/\lambda$, the average value of **Z** is given by

$$\bar{\mathbf{Z}}=4\pi\mathbf{P}\frac{(n\lambda/2\pi)^2}{n^2-1}\exp(i\mathbf{K}\cdot\mathbf{x})\ , \tag{A6}$$

leading to the average electric field[28]

$$\bar{\mathbf{E}}=\frac{4\pi}{n^2-1}[\mathbf{P}-n^2\mathbf{s}(\mathbf{P}\cdot\mathbf{s})]\exp(i\mathbf{K}\cdot\mathbf{x})\ , \tag{A7}$$

where $\mathbf{s}=\mathbf{K}/|\mathbf{K}|$. The macroscopic Maxwell field is often identified with an external applied field, which is completely unjustified. The macroscopic field is just that part of the internal field that depends on the retardation of the interaction.[29]

Long-wavelength limit

The terms with $\mathbf{y}(h)\neq0$ in (A5) describe the subtle periodic deviations from the average field. In the limiting case of long wavelength in which λ is much larger than the lattice constants, one is led to the electrostatic approximation and the deviation from the average field, $\mathbf{Z}'=\mathbf{Z}-\bar{\mathbf{Z}}$, is

$$\mathbf{Z}'(\mathbf{x})=\frac{4\pi}{V}\sum_k\mathbf{p}(k)\sum_h{}'\frac{\exp\{i\mathbf{y}(h)\cdot[\mathbf{x}-\mathbf{x}(k)]\}}{y(h)^2}\ , \tag{A8}$$

where $\sum_h'$ denotes the sum over all lattice vectors in reciprocal space except $\mathbf{y}(h)=0$.

Exciting field

The series (A8) is only conditionally convergent. Ewald solved this difficulty by transforming (A8) into two rapidly converging series: one series over direct and another over reciprocal space. In order to find the field at the position of a dipole, the infinite self-field has to be subtracted. Performing the differentiation and making the limiting transition $\mathbf{x}\rightarrow\mathbf{x}(k)$ gives the exciting field $\mathbf{E}(k)$ decomposed into the macroscopic Maxwell field $\overline{\mathbf{E}}$ and an inner field $\sum_{k'}\mathrm{Q}(kk')\mathbf{p}(k')$ as expressed in Eq. (2).

The local field tensors are defined by

$$Q_{\alpha\beta}(kk')=\frac{\partial^2}{\partial x_\alpha \partial x_\beta}\sum_l{}' \frac{1}{|\mathbf{x}|}\bigg|_{\mathbf{x}=\mathbf{x}(lk,k')} , \tag{A9}$$

where the prime in the summation denotes that the term $x(lk,k')=0$ has to be omitted. The explicit result is found, e.g., in Refs. 16 and 29.

Self-consistency condition

In the consistently microscopic theory, no use is made of the phenomenological material equation (7). Substitution of (A7) into (5) and neglecting the very small phase changes in $\exp(i\mathbf{K}\cdot\mathbf{x})$ gives an equation of self-consistency for $\mathbf{P}$. When $\mathbf{s}$ is parallel to one of the principle dielectric axes, $\mathbf{P}\cdot\mathbf{s}$ vanishes; it simplifies to

$$\sum_\beta \frac{4\pi}{V}\sum_{k,k'}[R_{\alpha\beta}(kk')-(n^2-1)\delta_{\alpha\beta}]P_\beta=0 , \tag{A10}$$

and the problem of determining the possible electromagnetic field in the crystal is reduced to an eigenvalue problem. The condition that the determinant of (A10) must be zero in general yields three distinct values for (n^2-1), to each of which corresponds an eigenvector $\mathbf{P}$.

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