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Nature of Ionic Deformations in Crystals; Application to an Analysis of the Magnetic Properties of the Alkali-Halide and Alkaline-Earth Oxide Crystals

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Absolute diamagnetic susceptibilities for the alkali-halide crystals are obtained theoretically and compared with the observed magnetic susceptibilities of these crystals in order to determine the crystalline paramagnetic susceptibilities. The paramagnetic susceptibilities obtained in this way are found to obey the linear relationship $\chi_{\text{para}}=0.11\ \chi_{\text{dia}}$. Theoretical analysis confirms this relationship for the alkali halides and indicates, in addition, that (1) Virtually all of the increased kinetic energy which the ions acquire in the process of crystallization takes the form of rotational kinetic energy; (2) the angular deformations of the ions in all the alkali halides are the same in that the average eigenvalue of the square of the angular momentum operator per electronic orbital is constant for all these crystals; and (3) the general relationship between χ_{dia} and χ_{para} for an ionic crystal is of the form $\chi_{\text{para}}=C\chi_{\text{dia}}$, where C is very nearly proportional to the average cohesive energy per ion of the crystal. The last conclusion is confirmed in the alkaline-earth oxides where $C\approx0.5$, in accord with the fact that the cohesive energies of these crystals are about five times those of the alkali halides. Furthermore, this analysis indicates that an ionic crystal with a large enough cohesive energy is paramagnetic, in agreement with observation.

I. INTRODUCTION

MAGNETIC properties of ionic crystals having a nondegenerate ground state have interested many investigators for several decades. However, there has been, to date, little success in the development of a fundamental understanding of the nature of the feeble magnetic susceptibilities which these crystals display. The observation that the magnetic susceptibilities of many materials of this type can be crudely approximated by the diamagnetic susceptibilities of their separate constituent ions has led to several attempts to interpret the crystalline magnetic properties by means of the additivity rule. These attempts have all clearly demonstrated that even in the alkali-halide crystals, which most closely resemble the ionic-model prototype, the crystalline susceptibilities cannot be represented as the additive sum of unchanging ionic diamagnetic susceptibilities. The attempts to relate ionic and crystalline magnetic susceptibilities in this manner have been summarized in a review article by Myers.[1]

The analysis of the magnetic properties of these materials is further confounded by the observation that many of them, such as some transition metal oxides, actually display a paramagnetic rather than a diamagnetic susceptibility.[2] This is a consequence of a fact which has been recognized for some time, namely, that the measured susceptibility of any such ionic crystal is a sum of two components, the diamagnetic susceptibility and the Van Vleck paramagnetic susceptibility, which are opposite in sign.[2] Moreover, since both components are temperature-independent, there is no way of experimentally determining their magnitudes separately. It is evident, therefore, that a fruitful analysis of the magnetic susceptibilities of ionic crystals must provide a thorough understanding of the nature of these two components.

An analysis of this type must concern itself with the nature of the deformations which the ions experience when transported into the crystal. These deformations may be placed into two different categories, namely, the radial deformations and the nonspherical or angular deformations. The deformation of the radial part of the ionic wave function yields changes in the ionic diamagnetic susceptibility; the nonspherical deformation of the ionic wave function produces a nonvanishing Van Vleck paramagnetism.

In the past, considerable attention has been given to the radial deformations, particularly in their effect upon the ionic polarizabilities and radii. A detailed analysis distinguishing the refraction of ions in the free gaseous state, solutions, and crystals was made long ago by Fajans and Joos,[3] who first suggested a contraction of the halogen ions and an expansion of the alkali ions in the alkali halides in passing from the free-ion state to the crystal. These conclusions are directly confirmed by comparison of the Pauling[4] free-ion polarizabilities with those determined by the least-squares technique from crystalline refractivities by Tessman, Kahn, and Shockley.[5] Subsequent calculations[6–8] have more or less established that the failure of the additivity rule for the ionic crystals is a result of the corresponding increase and decrease of the polarizabilities of the cations and anions, respectively, in the crystal brought about by the influence of the Madelung potential. Similar conclusions have been arrived at with respect to the

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[1] W. R. Myers, Rev. Mod. Phys. **24**, 15 (1952).

[2] See, for example, F. A. Grant, Rev. Mod. Phys. **31**, 646 (1959).

[3] K. Fajans and G. Joos, Z. Physik **23**, 1 (1924).

[4] L. Pauling, Proc. Roy. Soc. (London) **A114**, 191 (1927).

[5] J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).

[6] K. Fajans, Z. Physik Chem. **130**, 724 (1927).

[7] A. R. Ruffa, Phys. Rev. **130**, 1412 (1963).

[8] A. R. Ruffa, Phys. Rev. **133**, A1418 (1964).

nonadditivity of the ionic radii.[9,10] Similar conclusions with regard to the ionic diamagnetic susceptibilities are made in the Appendix by an analysis which parallels that of Ref. 7.

In contrast, the problem of developing an understanding of the ionic paramagnetic susceptibilities in crystals requires a more detailed understanding of the nature of the radial expansion and contraction of the electronic charge clouds of the ions, as well as their nonspherical deformations.

In this work, this problem will be attacked from two different points of view. In Sec. II, a detailed calculational procedure for determining absolute values for the diamagnetic susceptibilities of the alkali-halide crystals from existing optical data is presented. These absolute values are compared with the observed susceptibilities of the alkali halides in order to obtain semi-empirical values for the paramagnetic susceptibilities of these crystals. The values of the paramagnetic susceptibilities obtained in this way are found to display a simple relationship with the values of the crystalline diamagnetic susceptibilities.

In Sec. III, the problem is approached from a more fundamental point of view. The relationship between the crystalline cohesive energy and the rotational kinetic energy of the ions brought about by their nonspherical deformation is established. In particular, it is shown that the change in kinetic energy in the alkali halides produced by the radial deformation effects discussed above cancel. This information is used to obtain a theoretical equation for the paramagnetic susceptibilities of ionic crystals which is used to estimate a quantitative relationship between the paramagnetic and diamagnetic susceptibilities of the alkali halides. The result is found to agree favorably with the trend displayed by the semiempirically determined values obtained in Sec. II. In addition, some general conclusions are drawn regarding the paramagnetic susceptibilities of other ionic crystals, and, in particular, isoatomic sequences of ionic compounds. These conclusions are confirmed in the case of the alkaline-earth oxides.

II. CALCULATION OF THE DIAMAGNETIC SUSCEPTIBILITIES OF THE ALKALI-HALIDE CRYSTALS

The starting point for our calculation is an equation derived independently by Kirkwood and Vinti[11] which relates the diamagnetic susceptibility to the electric polarizability. The complete equation as given by Vinti is

$$|\chi_{\mathrm{dia}}| = (e^2 a_0^{1/2}/4mc^2)(N\alpha)^{1/2} - (e^2 L/6mc^2)\sigma\,, \qquad (1)$$

where α is the observed electric polarizability, N is the total number of electrons, a_0 is the Bohr radius, and L is Avogadro's number. The Kirkwood formula, which arbitrarily neglects the second term proportional to σ (see Appendix), was derived by the use of the variational theorem, while Vinti derived (1) by setting the quantity $\bar{E}_2$ discussed in the Appendix equal to $\bar{E}_3$ which appears in the relation for the electric polarizability obtained from second-order perturbation theory. As Vinti pointed out, the use of the variational procedure always yields a calculated diamagnetic susceptibility which is larger than the true susceptibility.[12] This is in agreement with the analysis[7] which demonstrates that $\bar{E}_2$ is always larger than $\bar{E}_3$. On the other hand, since the electrons repel each other, the average angle between any two radius vectors $\mathbf{r}_i$ and $\mathbf{r}_j$ is greater than $\pi/2$, so that σ is a negative quantity. This means that the exclusion of the second term in (1) results in an error which, because it gives a susceptibility smaller than that given by the complete formula, counteracts the inherent error in (1) which is brought about by the use of the variational procedure.

Therefore, the starting point for our calculations will be the Kirkwood formula

$$|\chi_{\mathrm{dia}}| = (e^2 a_0^{1/2}/4mc^2)(N\alpha)^{1/2}\,, \qquad (2)$$

which, incidently, can be obtained directly from Vinti's derivation by using the sum rule (A4) in the Appendix instead of (A1), and assuming that $\bar{E}_v = \bar{E}_1$, instead of $\bar{E}_2 = \bar{E}_3$. The aim behind the use of this formula lies in the expectation that the two errors inherent in it will cancel to a great degree. To test this premise, and the extent to which it fails, we now use (2) to calculate the diamagnetic susceptibilities of the rare gases. Table I displays the molar susceptibilities of five rare gases calculated by means of Eq. (2) together with the observed susceptibilities. The experimental values for α necessary to complete the calculation were obtained from the mole refraction data of Cuthbertson and Cuthbertson[13] extrapolated to infinite wavelength by Born and Heisenberg.[14] The mole refraction R_M is re-

TABLE I. Calculated and observed diamagnetic susceptibilities χ for the n-electron rare gases in 10^{-6} emu/mole. α_M is the molar electric polarizability and K_n is a correction factor in $|\chi_{\mathrm{dia}}|_{\mathrm{obs}} = (1+K_n)\times|\chi_{\mathrm{dia}}|_{\mathrm{calc}}$.

	n	α_M (Å^3)	$\lvert\chi_{\mathrm{dia}}\rvert_{\mathrm{calc}}$	$\lvert\chi_{\mathrm{dia}}\rvert_{\mathrm{obs}}$	K_n
He	2	0.203	1.97	1.88	−0.046
Ne	10	0.394	6.14	6.74	+0.098
A	18	1.636	16.76	19.57	+0.168
Kr	36	2.475	29.01	28.83	−0.006
Xe	54	4.023	45.50	43.85	−0.036

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[9] K. Fajans and H. Grimm, Z. Physik **2**, 299 (1920).

[10] F. G. Fumi and M. P. Tosi, J. Phys. Chem. Solids **25**, 31 (1964); M. P. Tosi and F. G. Fumi, *ibid.* **25**, 45 (1964). See also M. P. Tosi, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. 16.

[11] J. G. Kirkwood, Physik. Z. **33**, 37 (1932); J. P. Vinti, Phys. Rev. **41**, 813 (1932).

[12] This is a result of the fact that the true energy of the system always has a lower value than that obtained from the variational procedure.

[13] C. Cuthbertson and M. Cuthbertson, Proc. Roy. Soc. (London) **A84**, 13 (1911).

[14] M. Born and W. Heisenberg, Z. Physik **23**, 388 (1924).

lated to α_M in a gaseous material by the Lorentz relation

$$R_M=(4\pi L/3)\alpha_M. \tag{3}$$

The observed magnetic susceptibilities, which, because of the spherical symmetry of rare-gas atoms are all completely composed of the diamagnetic component, are taken from a compilation by Foëx.[15] These values represent an average of all experimental values reported, with the greatest weight given to the most reliable values.

The last column in Table I gives the fraction K_n by which the calculated susceptibility of the n-electron rare gas must be raised or lowered to make it correspond to the observed value, i.e., $|\chi_{\mathrm{dia}}|_{\mathrm{obs}}=(1+K_n)\times|\chi_{\mathrm{dia}}|_{\mathrm{calc}}$. The sign and magnitude of K_n is a measure of the degree to which the error in excluding the σ contribution exceeds or is exceeded by the use of the variational procedure, or equivalently, the $\bar{E}_2=\bar{E}_3$ approximation. A positive K_n indicates that the dominant error results from the exclusion of the σ contribution, while a negative sign points to the $\bar{E}_2=\bar{E}_3$ approximation as the larger source of error.

As can be seen from the values of K_n in Table I, the differences between the calculated and observed susceptibilities are under 10%, with the single exception of the 18-electron argon configuration where the calculated susceptibility is almost 17% too small. These differences, while not excessively large, exceed in many cases, as we shall see later, the magnitudes of the paramagnetic susceptibilities that we wish to determine. It is evident that if we wish to ascertain these relatively small paramagnetic susceptibilities of the alkali halides to any degree of reliability by subtracting the observed susceptibilities from the calculated diamagnetic susceptibilities the calculated values can contain an error of a few percent, at most. Consequently, the straight application of Eq. (2) is not sufficiently accurate for our purposes, and a means of correcting the values calculated in this manner is required. In order to do this, one can use the values of K_n obtained from the rare-gas calculations to correct the calculated alkali-halide diamagnetic susceptibilities, thus bringing the final result within the desired degree of accuracy. This may be accomplished after recognizing that the correction factor K_n associated with the n-electron rare gas is essentially the same as that for the positive or negative ion in the crystal having the n-electron rare-gas configuration.

Let us examine in detail why this is true. As was discussed above, Eq. (2) is based upon the assumption that $\bar{E}_v=\bar{E}_1$. Consequently, the equation is in error by the factor $\bar{E}_v/\bar{E}_1$, i.e., $\bar{E}_v/\bar{E}_1=(1+K_n)$. Because the various $\bar{E}$'s represent different averaging procedures for quantum-mechanical sums involving a given electronic configuration, it is concluded in the Appendix that ratios of these quantities do not differ greatly from unity and should be slowly varying functions of any effects which result from perturbation of the configuration. For this reason, assigning the same value of $\bar{E}_1/\bar{E}_v$ to both a free alkali or halide ion and the corresponding neutral rare-gas atom appears to be a fairly good approximation. However, it should be an even better approximation when considering the ions in the crystalline environment, since the Madelung potential has the effect of counteracting the excess or deficiency of nuclear charge in the cation and anion, respectively, as compared to the corresponding neutral rare-gas atom. Therefore, from here on, we will use the simplifying but fairly good approximation that the K_n for the ions in the crystal are the same as those for the corresponding rare-gas atom.

TABLE II. Calculated diamagnetic susceptibilities and observed susceptibilities for the alkali halides in 10^{-6} emu/mole. The number of electrons per molecule is n_1+n_2 and the molar electric polarizability is α_M.

	n_1+n_2	$\alpha_M(\mathrm{\AA}^3)$	$\lvert\chi_{\mathrm{dia}}\rvert_{\mathrm{calc}}$	$\lvert\chi_{\mathrm{dia}}\rvert_{\mathrm{calc}}{}^{\mathrm{corr}}$	$\lvert\chi_{\mathrm{obs}}\rvert$	χ_{para}
LiF	12	0.909	10.2	11.1	10.1	1.0
LiCl	20	2.903	23.5	27.3	24.3	3.0
LiBr	38	4.138	38.6	38.3	34.7	3.6
LiI	56	6.226	57.7	55.6	50	5.6
NaF	20	1.163	14.9	16.4	16.4	0.0
NaCl	28	3.263	29.5	34.1	30.3	3.8
NaBr	46	4.388	43.9	44.1	41	3.1
NaI	64	6.264	61.7	60.0	57.0	3.0
KF	28	2.008	23.2	26.5	23.6	2.9'
KCl	36	4.173	38.0	44.4	39.0	5.4
KBr	54	5.293	52.2	54.7	49.1	5.6
KI	72	7.388	71.3	72.0	63.8	8.2
RbF	46	2.572	33.6	34.4	31.9	2.5
RbCl	54	4.712	49.1	53.1	46	7.1
RbBr	72	5.920	63.6	63.2	56.4	6.8
RbI	90	8.093	83.3	81.1	72.2	8.9
CsF	64	3.604	46.9	46.4	44.5	1.9
CsCl[a]	72	5.829	63.3	66.1	56.7	9.4
CsBr[a]	90	7.020	77.5	75.9	67.2	8.7
CsI[a]	108	9.119	96.9	93.4	82.6	10.8

[a] CsCl structure.

The correction of the calculated diamagnetic susceptibilities of the alkali halides obtained from Eq. (2) may be accomplished, then, by the use of the K_n in Table II, weighted by the relative contribution of each type of ion to the total diamagnetic susceptibility, i.e.,

$$|\chi_{\mathrm{dia}}|_{\mathrm{calc}}{}^{\mathrm{corr}}=\Big(1+\sum_i \chi_{\mathrm{dia}}{}^{i}K_{ni}\Big/\sum_i \chi_{\mathrm{dia}}{}^{i}\Big)|\chi_{\mathrm{dia}}|_{\mathrm{calc}}, \tag{4}$$

where the index i refers to the ith ionic species in the crystal, and $|\chi_{\mathrm{dia}}|_{\mathrm{calc}}$ is obtained directly from Eq. (2). For binary compounds such as the alkali halides, this formula has the simpler form

$$|\chi_{\mathrm{dia}}|_{\mathrm{calc}}{}^{\mathrm{corr}}=\left(1+\frac{\chi_{\mathrm{dia}}{}^{\mathrm{anion}}K_n{}^{\mathrm{anion}}+\chi_{\mathrm{dia}}{}^{\mathrm{cation}}K_n{}^{\mathrm{cation}}}{\chi_{\mathrm{dia}}{}^{\mathrm{anion}}\chi_{\mathrm{dia}}{}^{\mathrm{cation}}}\right)\times|\chi_{\mathrm{dia}}|_{\mathrm{calc}}. \tag{5}$$

The results of the calculations on the alkali halides are listed in Table II. The first column lists the total number of electrons in the two-ion molecular group, while the second column gives the molecular polariza-

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[15] G. Foëx, in *Tables de Constantes et Données Numériques*, (Mason & Cie., Paris, 1957), No. 7.

bility for infinite wavelength listed by Tessman, Kahn, and Shockley.[5] The next column lists the molar crystalline diamagnetic susceptibility $|\chi_{\text{dia}}|_{\text{calc}}$ obtained from these polarizabilities and Eq. (2). The fourth column contains the values of $|\chi_{\text{dia}}|_{\text{calc}}^{\text{corr}}$ calculated by means of Eq. (5). The ionic diamagnetic susceptibilities necessary to complete the calculation were obtained by substituting the ionic polarizabilities computed in Ref. 7 into Eq. (5) and correcting the result by means of the appropriate K_n's in Table II. The next column lists the observed magnetic susceptibilities which are again taken from Ref. 15, while the last column gives the values of the crystalline paramagnetic susceptibilities where

$$\chi_{\text{para}} = |\chi_{\text{dia}}|_{\text{calc}}^{\text{corr}} - |\chi_{\text{obs}}|\,.$$

Before analyzing the results, let us first estimate the degree of accuracy of the listed crystalline paramagnetic susceptibilities. There are four major sources of error in these values. They are:

1. The observed magnetic susceptibilities. Since few of the reported values of the crystalline susceptibilities agree to within 1%, the errors in the observed values listed in Ref. 15 are probably of the order of 2 to 3%;
2. The observed refractive indices. While refractive indices can be measured to a high degree of accuracy, the extrapolation procedure for obtaining the refractive index at infinite wavelength probably contains an error of the order of 3% of the extrapolated value;
3. The correction factors K_n. These are strongly dependent upon the observed diamagnetic susceptibilities of the rare gases which display a considerable spread in the reported values. Because of this, the K_n can be in error by as much as 20%, which could contribute an error in a calculated ionic susceptibility of as much as 3 or 4%. We assume that the errors associated with the use of the rare-gas K_n's for the ions are of a much smaller magnitude and, therefore, do not appreciably change this error estimate.
4. The computed ionic diamagnetic susceptibilities used in correcting the calculated crystalline diamagnetic susceptibility. The computed ionic polarizabilities fail to reproduce the observed values by as much as 20%, so that the similar failure of the ionic diamagnetic susceptibilities based on these values is as much as 10%. However, only the relative values of the ionic diamagnetic susceptibilities enter into the correction in Eq. (5). Because of this, and the fact that the relative values of the ionic diamagnetic susceptibilities are only used to weight the correction factors, this is the smallest of the major sources of error, and contributes no more than 1 to 2% to the total.

The total of these errors can be as much as 10% of the value of $|\chi_{\text{dia}}|_{\text{calc}}^{\text{corr}}$. As will be seen below, this is equivalent to about a 100% uncertainty in χ_{para}. Fortunately, however, these errors are independent of each other, and are therefore not strictly additive. In most cases, they will partially or almost completely cancel. Consequently, there is a large uncertainty in the precision of each individual value of χ_{para}, but because of the random nature of the above-discussed errors, the over-all trend of the values can be established.

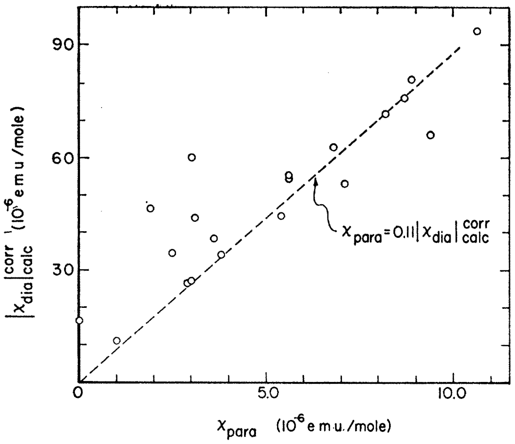

FIG. 1. Theoretical diamagnetic susceptibility versus semi-empirical paramagnetic susceptibility for the alkali-halide crystals.

The over-all trend can be observed by comparing the values of χ_{para} and $|\chi_{\text{dia}}|_{\text{calc}}^{\text{corr}}$ in Table II. First, from the above discussion, one would expect the diamagnetic susceptibility to be larger than the observed susceptibility because of the canceling effect of the paramagnetic susceptibility. This is invariably the case with the single exception of NaF, where the two quantities are equal and therefore yield a vanishing χ_{para}. Otherwise, the values of χ_{para} seem to be approximately proportional to the values of $|\chi_{\text{dia}}|_{\text{calc}}^{\text{corr}}$, their ratio being about 1/10. A plot of χ_{para} versus $|\chi_{\text{dia}}|_{\text{calc}}^{\text{corr}}$ in Fig. 1 confirms this conclusion. Although there is considerable scatter in the points, they seem to be best represented by the linear relationship $\chi_{\text{para}} = 0.11|\chi_{\text{dia}}|_{\text{calc}}^{\text{corr}}$.

This conclusion contains the implicit assumption that the curve must pass through the origin, i.e., that the deformation effects which produce the paramagnetism do not vanish for some nonvanishing value of the diamagnetic susceptibility. The null value of χ_{para} in the case of NaF seems to correspond to the case of the 10% error in the values of $|\chi_{\text{dia}}|_{\text{calc}}^{\text{corr}}$ and $|\chi|_{\text{obs}}$, while the large scatter in the points is another manifestation of the inherent errors in the results.

Through the process of inference, we have arrived at what appears to be the first demonstration of the paramagnetic properties of the alkali-halide crystals. In the next section, a theoretical analysis will be made in an attempt both to understand this result and to generalize upon it.

III. THE NATURE OF THE PARAMAGNETISM OF IONIC CRYSTALS

According to a detailed discussion given previously,[8] the paramagnetic susceptibility of an ionic crystal can be expressed in the form

$$\chi_{\text{para}}=\frac{e^2}{6m^2c^2}\frac{1}{\bar{E}_M}\langle\gamma|(\sum_{j=1}^{N}\mathbf{L}_j)^2|\gamma\rangle$$
$$=\frac{e^2}{6m^2c^2}\frac{1}{\bar{E}_M}\sum_{i=1}^{M}\langle\gamma|\mathbf{L}_i^2|\gamma\rangle, \quad (6)$$

where $\bar{E}_M$ is the magnetic mean excitation energy defined in Ref. 8, and

$$\mathbf{L}_i^2=(\sum_{j=1}^{n^i}\mathbf{L}_j)^2,$$

where L_j operates only on electron j. The system of separated ions displays no paramagnetism since all of the ions have spherically symmetric probability amplitudes, and consequently all the $\langle\gamma|\mathbf{L}_i^2|\gamma\rangle$ vanish. The crystalline environment, in contrast, imposes a perturbation upon the ions which has symmetry properties more restricted than those of the full rotation group, so that the complete spherical symmetry of the ionic probability amplitudes is destroyed. The paramagnetism then arises from the nonvanishing $\langle\gamma|\mathbf{L}_i^2|\gamma\rangle$.

In this section, we will examine the nature of the paramagnetism from a theoretical point of view. The aim of this analysis is twofold. First, we wish to quantitively verify by theoretical means the relationship between the diamagnetic and paramagnetic susceptibilities of the alkali halides obtained semiempirically in the previous section. Second, we wish to generalize upon this result for application to other ionic crystals. To accomplish these aims, we will attempt to examine the form of the ionic wave function in the crystal and the manner in which the paramagnetic susceptibility given by Eq. (6) arises from it. Because of the complexity of the problem, the analysis will rely upon a physical model which is necessarily approximate. However, it is hoped that the model will be sufficiently realistic to yield the main features of the paramagnetism of ionic crystals which have been determined from the examination of experimental data.

Our analysis will again be made within the framework of the product approximation. Let us denote by $\Psi_i^{(0)}$ and Ψ_i the wave functions for the ith free ion and the corresponding ion in the crystal, respectively. It is convenient in examining the nature of Ψ_i and its relationship with $\Psi_i^{(0)}$ to define a one-particle probability amplitude $\gamma(\mathbf{x}_1)$ given by

$$\gamma^*(\mathbf{x}_1)\gamma(\mathbf{x}_1)=\gamma(\mathbf{x}_1|\mathbf{x}_1), \quad (7)$$

where $\gamma(\mathbf{x}_1|\mathbf{x}_1)$ is a diagonal element of the one-particle density matrix given by

$$\gamma(\mathbf{x}_1|\mathbf{x}_1)=N\int\Psi^*(\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_N)$$
$$\times\Psi(\mathbf{x}_1\mathbf{x}_2\cdots\mathbf{x}_N)d\mathbf{x}_2\cdots d\mathbf{x}_N. \quad (8)$$

The integration over coordinate $\mathbf{x}_1$ in (8) is omitted. Defined in this manner, $\gamma^*(\mathbf{x}_1)\gamma(\mathbf{x}_1)$ represents a number density, which means that $\gamma^*(\mathbf{x}_1)\gamma(\mathbf{x}_1)dv_1=$ number of particles times the probability of finding a particle within a volume dv_1 about $\mathbf{x}_1$ when the coordinates of all the other particles remain arbitrary. This definition of $\gamma(\mathbf{x}_1)$ requires that

$$\int\gamma^*(\mathbf{x}_1)\gamma(\mathbf{x}_1)dx_1=N. \quad (9)$$

It is evident that the properties of $N^{-1/2}\gamma(\mathbf{x}_1)$ are analogous to those of a one-particle wave function normalized to unity.

The one-particle probability amplitude $\gamma_i^{(0)}(\mathbf{r}_1)$ associated with $\Psi_i^{(0)}$ is spherically symmetric, while $\gamma_i(\mathbf{x}_1)$ associated with Ψ_i is not. Instead, $\gamma_i(\mathbf{x}_1)$ must have the point symmetry of the crystalline environment surrounding the ion. Accordingly, $\gamma_i(\mathbf{x}_1)$ can be written in the form

$$\gamma_i(\mathbf{x}_1)=\gamma_i^{(0)}(\mathbf{r}_1)+f_i(\mathbf{r}_1)\sum_{l,m}b_{lm}(i)Y_{lm}(\theta_1\Phi_1), \quad (10)$$

where the $b_{lm}(i)$ are normalization constants. The spin coordinates are ignored in (10) since the total spin for each of the ions is zero. The number of spherical harmonics $Y_{lm}(\theta_1,\Phi_1)$ which appear in the sum is restricted by the condition that each of them must be consistent with the required point symmetry.

The determination of the analytical form of the $\gamma_i(\mathbf{x}_1)$'s in Eq. (10) is extremely difficult since neither the $\gamma_i^{(0)}(\mathbf{r}_1)$'s nor the detailed form of the crystalline perturbing potential have been determined to any degree of accuracy. Because of this fact, we will try instead an alternate mode of theoretical analysis. By relying heavily upon inferences drawn from the physical nature of the ionic crystals, we will attempt to ascertain those features of the $\gamma_i(\mathbf{x}_1)$'s which are important to the determination of the paramagnetic susceptibilities without resorting to detailed studies of their complete analytic properties.

We begin by writing the N-particle Hamiltonian for the system in the following manner:

$$\mathbf{H}=\sum_{j=1}^{N}\left\{\frac{-\hbar^2}{2mr_j^2}\frac{\partial}{\partial r_j}\left(r_j^2\frac{\partial}{\partial r_j}\right)+\frac{\mathbf{L}_j^2}{2mr_j^2}\right\}$$
$$+V(\mathbf{r}_1\mathbf{r}_2\cdots\mathbf{r}_N), \quad (11)$$

where the first two terms are the radial and rotational or angular kinetic-energy operators, respectively. Since the potential-energy term includes only Coulombic interactions, the virial theorem is applicable. Therefore, the change in the total energy of the system brought about by the crystallization of the free-ion system, i.e., the cohesive energy E_c, is equal to the negative of the change in the total kinetic energy. Based upon the form of the Hamiltonian (11), this may be expressed as

$$-E_c = \Delta T_{\mathrm{rad}} + \Delta T_{\mathrm{ang}}, \qquad (12)$$

where ΔT_{rad} and $\Delta T_{\mathrm{ang}} = T_{\mathrm{ang}}$ are the changes in the radial and angular components of the kinetic energy.

Because we wish to eventually develop a mathematical relation between T_{ang} and χ_{para}, it is necessary to make a quantitative estimate of the relative magnitudes of ΔT_{rad} and T_{ang}. This requires that we know something about the radial dependences of the angular deformations of the ionic probability amplitudes, which in turn requires a more detailed picture of the crystalline interaction than is available. Because of this, we propose a simple model in order to obtain the desired relationship. Because of the extreme simplicity of the model used, the result will not be presented as a rigorously proven fact, but rather, one which will be used for calculational convenience.

Previous calculations[7] have linked the change in the ionic polarizabilities in the alkali halides with the Madelung potential. The discussion in the Appendix does the same in the case of the ionic diamagnetic susceptibilities. This suggests that a simple discussion of the effect of the crystalline environment upon the ionic radial wave functions can be made in terms of the point-charge potential of the surrounding charged ions.

Such an approach presents many problems, the most important of which is the fact that the integrated average potential of an assembly of point charges over the surface of a sphere is independent of the diameter of the sphere, as long as the charges remain outside the sphere. Under this condition, on the average, there would be no radial force on the ionic electrons under consideration, so that the radial expansion and contraction of the anions and cations discussed above could not be accounted for by this model unless the probability amplitude of the ion in question extends appreciably beyond the nearest-neighbor distance. The results of later calculations indicate, however, that this does happen. Therefore, we will assume at this point, in accord with the simple model, that the extension of the ionic probability amplitudes beyond the nearest-neighbor distance is the mechanism by which the point-charge potential contract or expands the radial probability amplitudes of the ions.

This leads to two conclusions. First, only the tails of the outer orbitals of the ions are appreciably perturbed according to this model. Second, the perturbation should be produced primarily by the nearest neighbors, since the next nearest-neighbor positions are presumably too far away for the probability amplitudes to have any appreciable magnitude there.

In order to make detailed evaluation of ΔT_{rad}, ΔT_{ang}, and ultimately, the crystalline paramagnetic susceptibility, we must translate these ideas into specific analytic properties of the $\gamma_i(\mathbf{x}_1)$ in Eq. (10). To begin with, we assume that the number of electrons in the ions is conserved. Consequently, the normalization condition (9) yields the relations

$$\int |\gamma_i^{(0)}(\mathbf{r}_1)|^2 \mathbf{r}_1^2 d\mathbf{r}_1 = n_i \qquad (13)$$

and

$$\int |\gamma_i(\mathbf{x}_1)|^2 d\mathbf{x}_1 = n_i, \qquad (14)$$

where n_i is the number of electrons in the ith ion. If we make use of (13) and the specific form of $\gamma_i(\mathbf{x}_1)$ in Eq. (10), then the normalization condition (14) reduces to

$$\sum_{l,m} |b_{lm}(i)|^2 \int_0^\infty |f_i(\mathbf{r}_1)|^2 \mathbf{r}_1^2 d\mathbf{r}_1 + 2b_{00} \int_0^\infty f_i(\mathbf{r}_1)\gamma_i^{(0)}(\mathbf{r}_1)\mathbf{r}_1^2 d\mathbf{r}_1 = 0. \qquad (15)$$

The physical meaning of (15) is simple. Since the total number of electrons is conserved, any increase in the ionic electron density at one point brought about by the crystalline potential must be compensated for by a corresponding decrease in the electron density at some other point. We concluded earlier that only the outer portion of the outermost s and p orbitals of the ions were appreciably perturbed in the crystal. This means that $f_i(\mathbf{r}_1)$ is nonvanishing only at the tail end of $\gamma_i(\mathbf{x}_1)$. If we define a characteristic radius $\mathbf{r}_1 = \mathbf{r}_i^0$ about which the electron-density perturbation effects for the ith ion are centered, the integrand in Eq. (15) can be expressed in terms of a new radial variable $\mathbf{r}_1' = \mathbf{r}_1 - \mathbf{r}_i^0$, where $\mathbf{r}_1' \ll \mathbf{r}_i^0$:

$$g_i(\mathbf{r}_1') = |f_i(\mathbf{r}_1')|^2 \sum_{l,m} |b_{lm}(i)|^2 + 2b(i) f_i(\mathbf{r}_1')\gamma_i^{(0)}(\mathbf{r}_1'). \qquad (16)$$

The constant factor $\mathbf{r}_1^2 \approx (\mathbf{r}_i^0)^2$ in the integrand is not included in (16). To a first approximation, the radial function $g_i(\mathbf{r}_1')$ is an odd function, i.e., $g_i(-\mathbf{r}_1') = -g_i(\mathbf{r}_1')$. If an ion is subject to a positive Madelung potential, for example, then $g(\mathbf{r}_1')$ is positive for negative values of $\mathbf{r}_1'$ signifying that the electron density of the ion is increased for $\mathbf{r}_1 < \mathbf{r}_i^0$ and decreased for $\mathbf{r}_1 > \mathbf{r}_i^0$. The reverse is true for a negative Madelung potential. Consequently, we conclude that the sign of $g_i(\mathbf{r}_1')$ for $\mathbf{r}_1' > 0$ is the same as the sign of the Madelung potential acting upon the ion in question.

We now wish to estimate what fraction of the kinetic energy of crystallization should be attributed to its angular component. This can be done within the framework of our model if certain additional assumptions are made. These will be detailed as they become necessary.

In the alkali halides, where the positive- and negative-ion sites are geometrically equivalent, the perturbing influence of the point-charge potential should be nearly equal in magnitude but opposite in sign. This should be approximately true in all ionic crystals, since charge neutrality requires that each ion has nearest neighbors (or approximate nearest neighbors) such that the product of the total number of such neighbors and their net charge be constant. We label the magnitude of the point-charge potential acting in the region of appreciable ionic perturbation as V_M. We assume further that the radial region over which the potential acts is sufficiently localized so that V_M may be expressed as a sum of two potentials: the average over angular variables which will be designated as $V(R)$, and another potential $V(\theta,\Phi)$ which superimposes on $V(R)$ the required angular dependence of V_M. Since the behavior of $V(R)$ is essentially the same for both cations and anions with the exception of the sign difference, it should produce virtually no net change in the internal potential energy of the ions since the decrease in potential energy of the cations will be counterbalanced by a corresponding increase in the case of the anions.

The connection between this conclusion and the change in the radial kinetic energy is rather straightforward if, in addition to assuming that the ions maintain their individual identities, we also assume that all the potential-energy contributions in the system not included in the self-energy of the ions correspond to the cohesive energy of the crystal E_c.[16] In that case, the virial theorem requires that the total kinetic energy of the ions in the system must increase by an amount E_c, while the internal potential energy of the ions must be lowered by an amount E_c. According to this restriction, the fact that $V(R)$ produces no net change in the internal potential energy of the ions leads to the conclusion that it produces no net change in their kinetic energy as well. Since $V(R)$ only deforms the ions radially, this means that its action on the ions produces no net change in their radial kinetic energy.

The process of separating the Madelung potential into a sum of the two potentials discussed above is equivalent to expressing (10) in the form

$$\gamma_i(\mathbf{x}_1)=\bar{\gamma}_i^{(0)}(\mathbf{r}_1)+f_i(\mathbf{r}_1)\sum_{l\neq 0,m}\bar{b}_{lm}(i)Y_{lm}(\theta_1\Phi_1), \quad (17)$$

where $\bar{\gamma}_i^{(0)}(\mathbf{r}_1)$ is the one-particle probability amplitude produced by the action of $V(R)$ upon the free ion. We have seen that the radial kinetic energy of the system described by the $\bar{\gamma}_i^{(0)}(\mathbf{r}_1)$ is the same as that of the free-ion system described by the $\gamma_i^{(0)}(\mathbf{r}_1)$. It is evident from the normalization condition (15) and the form of $g(\mathbf{r}_1')$ in (16) that Eq. (17) requires that

$$\int_{-r_a}^{\infty}\bar{f}_i(\mathbf{r}_1')\bar{\gamma}_i^{(0)}(\mathbf{r}_1')(\mathbf{r}')^2d\mathbf{r}'=0 \quad (18)$$

and

$$\sum_{l\neq 0,m}|\bar{b}_{lm}(i)|^2=0. \quad (19)$$

It follows from the condition (19) that the expectation value of any purely radial operator evaluated by means of either $\gamma_i(\mathbf{x}_1)$ or $\bar{\gamma}_i^{(0)}(\mathbf{r}_1)$ must be the same. From this we conclude that the expectation value of the radial kinetic energy is the same when the system is described by either the $\gamma_i(\mathbf{x}_1)$ or the $\gamma_i^{(0)}(\mathbf{r}_1)$. Therefore, there is no change in the radial kinetic energy of the system produced by the point-charge potential.

The use of this model has led to a very simple conclusion, namely, that the angular component of the kinetic energy of crystallization, which because of the spherical symmetry of the free ions must represent the total angular kinetic energy of the system, is equal in magnitude to E_c. It is evident, however, that the model, itself, is a great oversimplification of the actual situation. The use of the point-charge potential alone to represent the interaction of the crystalline environment upon an ion completely overlooks both the short-range exchange potential between ions and the short-range correction to the Madelung potential. The latter, in particular, would appear to be important, since such extreme penetration of the surrounding electronic charge clouds of the surrounding ions by the probability amplitude of a given ion to the extent postulated by the model would appear to raise considerable doubt as to just what the effective charges of the surrounding ions really is. In order that the point-charge model be reasonably valid, it is necessary that the short-range corrections to the Madelung potential cancel on the average. It is not immediately apparent why they should do this, but the success of the earlier analysis of the ionic polarizabilities in terms of the Madelung potential suggests that the associated radial deformations may indeed result from such a mechanism.

We will proceed from here on the assumption that the magnitude of the angular kinetic energy of the system is equal in magnitude to the crystalline cohesive energy. We have already noted that there is a close relationship between the ionic paramagnetism and the angular kinetic energy of the ions in the crystal. Consequently, this assumption implies a relationship between the ionic paramagnetic susceptibility and the cohesive energy. Subsequent calculations will be seen to be not inconsistent with this assumption. Because the development of an approximate form of this relationship is somewhat involved, we will first briefly sketch the argument.

The paramagnetic susceptibility (6) contains the quantity

$$\langle\gamma|(\sum_{j=1}^{N}\mathbf{L}_j)^2|\gamma\rangle,$$

which we would like to connect with the angular part of the Hamiltonian (11). To form the connection, it is

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[16] The individuality of the ions is equivalent to the product approximation. This approximation results in the energy of the system being expressible as a sum of ionic self-energy terms and ionic interaction terms (Ref. 7). The above assumption is equivalent to equating the ionic interaction terms with the cohesive energy of the crystal.

most convenient to relate both to a third quantity

$$\langle\gamma|\sum_{j=1}^{N}\mathbf{L}_j^2|\gamma\rangle.$$

We first obtain a useful expression for this quantity. By reference to earlier work and using Eqs. (6) and (A5) in the Appendix, we can then write the paramagnetic susceptibility in terms of this quantity and the diamagnetic susceptibility. Turning next to the cohesive energy, we obtain an expression for it in very similar but not quite identical form. Several simplifying assumptions are needed to reduce this expression to a form which can then be inserted into the equation for the ionic paramagnetic susceptibility. This yields, finally, the desired theoretical expression for the paramagnetic susceptibility of an ionic crystal.

We begin by obtaining an expression for

$$\langle\gamma|\sum_{j=1}^{N}\mathbf{L}_j^2|\gamma\rangle.$$

In the product approximation, the one-particle effects for the ions are strictly additive. Therefore,

$$\langle\gamma|\sum_{j=1}^{N}\mathbf{L}_j^2|\gamma\rangle=\sum_{i=1}^{M}\int\gamma_i^*(\mathbf{x}_1)\mathbf{L}_1^2\gamma_i(\mathbf{x}_1)d\mathbf{x}_1$$

$$=\frac{M}{t}\sum_{i=1}^{t}\int\gamma_i^*(\mathbf{x}_1)\mathbf{L}_1^2\gamma_i(\mathbf{x}_1)d\mathbf{x}_1, \quad (20)$$

where t is the number of different ionic species in the crystal or, more generally, the number of ions comprising the crystalline molecular group. If we now make use of (10), Eq. (20) becomes

$$\langle\gamma|\sum_{j=1}^{N}\mathbf{L}_j^2|\gamma\rangle=\frac{M}{t}\sum_{i=1}^{M}\sum_{l,m}|b_{lm}(i)|^2$$

$$\times l(l+1)\hbar^2\int_0^\infty|f_i(\mathbf{r}_1')|^2\mathbf{r}_1^2d\mathbf{r}_1. \quad (21)$$

For simplicity, we may rewrite (21) as

$$\langle\gamma|\sum_{j=1}^{N}\mathbf{L}_j^2|\gamma\rangle=\frac{M}{t}\sum_{i=1}^{M}n_i\lambda_i(\lambda_i+1)\hbar^2. \quad (22)$$

The relationship between

$$\langle\gamma|\sum_{i=1}^{N}\mathbf{L}_j^2|\gamma\rangle$$

and

$$\langle\gamma|(\sum_{j=1}^{N}\mathbf{L}_j)^2|\gamma\rangle,$$

which appears in Eq. (6) is not a simple one. However, it has been demonstrated[17] that when the cosines of the correlation angles discussed in the Appendix are small, then

$$\langle\gamma|\sum_{j=1}^{N}\mathbf{A}_j^2|\gamma\rangle/\langle\gamma|(\sum_{j=1}^{N}\mathbf{A}_j)^2|\gamma\rangle$$

$$\approx\langle\gamma|\sum_{j=1}^{N}\mathbf{B}_j^2|\gamma\rangle/\langle\gamma|(\sum_{j=1}^{N}\mathbf{B}_j)^2|\gamma\rangle, \quad (23)$$

where **A** and **B** are two different and arbitrary operators. By taking the ratios of Eqs. (A1) and (A5), one finds that

$$\langle\gamma|\sum_{j=1}^{N}\mathbf{r}_j^2|\gamma\rangle/\langle\gamma|(\sum_{j=1}^{N}\mathbf{r}_j)^2|\gamma\rangle=\bar{E}_2/\bar{E}_v. \quad (24)$$

Earlier calculations indicate that the ratio $\bar{E}_2/\bar{E}_v$ does not differ greatly from unity. Therefore, we conclude that the approximation (23) is valid in the cases under consideration here and that

$$\langle\gamma|\sum_{j=1}^{N}\mathbf{L}_j^2|\gamma\rangle/\langle\gamma|(\sum_{j=1}^{N}\mathbf{L}_j)^2|\gamma\rangle=\bar{E}_2/\bar{E}_v. \quad (25)$$

If we now compare Eq. (25) with (22), (6), and (A5), we see that the crystalline paramagnetic susceptibility can be written in the form

$$\chi_{\text{para}}=(e^2/6m^2c^2)(\bar{E}_v/\bar{E}_2\bar{E}_M)N\hbar^2\langle\lambda_i(\lambda_i+1)\rangle_{\text{av}}$$

$$=-(2\beta/3)\chi_{\text{dia}}\langle\lambda_i(\lambda_i+1)\rangle_{\text{av}}, \quad (26)$$

where $\beta=\bar{E}_v^2/\bar{E}_2\bar{E}_M$, and $\langle\lambda_i(\lambda_i+1)\rangle_{\text{av}}$ is an average value of the $\lambda_i(\lambda_i+1)$ for the different types of ions in the crystal given by

$$\langle\lambda_i(\lambda_i+1)\rangle_{\text{av}}=\sum_{i=1}n_i\lambda_i(\lambda_i+1)/\sum_{i=1}n_i. \quad (27)$$

In order to introduce the cohesive energy, we must relate it in the form of the angular component of the kinetic energy of the system to the quantity

$$\langle\gamma|\sum_{j=1}^{N}\mathbf{L}_j^2|\gamma\rangle.$$

Again using (10), the expectation value for the operator $\sum^{N}_{j=1}(\mathbf{L}_j^2/r_j^2)$ is found to be

$$\langle\gamma|\sum_{j=1}^{N}(\mathbf{L}_j^2/r_j^2)|\gamma\rangle$$

$$=\frac{M}{t}\sum_{i=1}^{t}\int\gamma_i^*(\mathbf{x}_1)(\mathbf{L}_1^2/r_1^2)\gamma_i(\mathbf{x}_1)d\mathbf{x}_1$$

$$=\frac{M}{t}\hbar^2\sum_{i=1}^{t}\int_0^\infty|f_i(\mathbf{r}_1)|^2d\mathbf{r}_1\sum_{l,m}|b_{lm}(i)|^2l(l+1). \quad (28)$$

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[17] A. R. Ruffa, J. Res. Natl. Bur. Std. (U. S.) **69A**, 167 (1965).

If we let

$$\langle r_i^2\rangle=\int_0^\infty \mathbf{r}_1^2|f_i(\mathbf{r}_1)|^2d\mathbf{r}_1\bigg/\int_0^\infty |f_i(\mathbf{r}_1)|^2d\mathbf{r}_1,$$

then it follows from (21), (28), and (32) that

$$\langle\gamma|\sum_{j=1}(\mathbf{L}_j^2/r_j^2)|\gamma\rangle$$

$$=(M/t)\hbar^2\sum_{i=1}^{t} n_i\lambda_i(\lambda_i+1)(\langle r_i^2\rangle)^{-1}. \quad (29)$$

We saw earlier that the angular component of the kinetic energy of the system is very nearly equal to $-E_c$. Consequently, Eq. (29) can be written as

$$-2mE_c{}^t=\hbar^2\sum_{i=1}^{t} n_i\lambda_i(\lambda_i+1)(\langle r_i^2\rangle)^{-1}, \quad (30)$$

where $E_c{}^t$ is the lattice energy for the crystalline molecular group. In the alkali halides, $E_c{}^t$ is simply the lattice energy per cation-anion pair.

In order to relate the result (30) to the crystalline paramagnetic susceptibility, we must perform the indicated summation—a task which presents grave difficulties. Consequently, we will make use of several simplifying approximations. First, let us rewrite (30) in the following form:

$$-2mE_c{}^t=\hbar^2\sum_{i=1}^{t} n_i\lambda_i(\lambda_i+1)[\eta_i\sum_{i=1}^{n_i}\langle\gamma|{}^i\mathbf{r}_j{}^2|\gamma\rangle]^{-1}, \quad (31)$$

where

$$\eta_i=\langle r_i^2\rangle/\sum_{j=1}^{n_i}\langle\gamma|{}^i\mathbf{r}_j{}^2|\gamma\rangle.$$

Taking advantage of Eq. (A5), (31) can be re-expressed as

$$-2mE_c{}^t=\hbar^2\sum_{i=1}^{t}\bar{E}_v{}^i\lambda_i(\lambda_i+1)\eta_i{}^{-1}, \quad (32)$$

where

$$\bar{E}_v{}^i=\frac{3\hbar^2}{2m}n_i/\sum_{j=1}^{n_i}\langle\gamma|{}^i\mathbf{r}_j{}^2|\gamma\rangle.$$

It was stated earlier that the $\bar{E}$'s for the different ions are made to converge to values which are not greatly different from each other by the action of the Madelung potential. This suggests that we may replace the $\bar{E}_v{}^i$ in (32) with their composite average for the crystal. If one makes the further simplifying assumptions that the η_i for the different ions are essentially the same and equal to their composite average value η, and that

$$\frac{1}{t}\sum_{i=1}^{t}\lambda_i(\lambda_i+1)\approx\langle\lambda_i(\lambda_i+1)\rangle_{\text{av}}, \quad (33)$$

one obtains the following expression for $\langle\lambda_i(\lambda_i+1)\rangle_{\text{av}}$:

$$\langle\lambda_i(\lambda_i+1)\rangle_{\text{av}}\approx-3\eta E_c{}^t/t\bar{E}_v, \quad (34)$$

where

$$\bar{E}_v=\frac{3\hbar^2}{2m}\sum_{i=1}^{t} n_i/\sum_{i=1}^{t}\sum_{j=1}^{n_i}\langle\gamma|{}^i\mathbf{r}_j{}^2|\gamma\rangle,$$

and

$$\eta=\sum_{i=1}^{t}\eta_i\sum_{j=1}^{n_i}\langle\gamma|i\mathbf{r}_j{}^2|\gamma\rangle/\sum_{i=1}^{t}\sum_{j=1}^{n_i}\langle\gamma|{}^i\mathbf{r}_j{}^2|\gamma\rangle.$$

Making use of (26) and (34), we obtain a theoretical expression for the paramagnetic susceptibility of the crystalline system:

$$\chi_{\text{para}}=(2\eta\beta E_c{}^t/t\bar{E}_v)|\chi_{\text{dia}}|. \quad (35)$$

In the alkali halides, $t=2$, so that (35) reduces to

$$\chi_{\text{para}}=(\eta\beta E_c{}^t/\bar{E}_v)|\chi_{\text{dia}}|.$$

Let us now examine the quantity $\eta\beta E_c{}^t/\bar{E}_v$ in detail. The lattice energies of the alkali halides are well known and vary between a minimum value of 6.2 eV per ion pair for CsI and a maximum value of 10.5 eV per ion pair for LiF. The quantity $\bar{E}_v$ can be determined from the calculated diamagnetic susceptibilities for the alkali halides in Table II. One may observe from this table that the numerical value of $|\chi_{\text{dia}}|$ in units of 10^{-6} emu/mole is approximately equal to n_1+n_2. Making use of Eq. (A6), one can conclude that $\bar{E}_v$ is nearly constant for these materials and is approximately equal to 32 eV. The quantities η and β are much more difficult to determine. Because of this, we will only attempt to make crude estimates of their values here.

In order to estimate the value of η, we must make an examination of the physical nature of $\langle r_i^2\rangle$. Since $f_i(\mathbf{r}_1')$ is centered about a radius $\mathbf{r}_i\gg\mathbf{r}_1'$,

$$\int_0^\infty \mathbf{r}_1^2|f_i(\mathbf{r}_1')|^2dr_1'\approx(\mathbf{r}_i)^2\int_0^\infty |f_i(\mathbf{r}_1')|^2d\mathbf{r}_1',$$

so that $\langle r_i^2\rangle\approx(\mathbf{r}_i)^2$. Because the perturbation effects are concentrated in the outer parts of the outer electronic orbitals, $(\mathbf{r}_i)^2$ is greater than the expectation value of the square of the electronic radius vector for any one of the outer orbitals. However, because these expectation values are nearly the same for each of the outer eight orbitals, and the sum of these is nearly equal to

$$\sum{}^{n_i}{}_{j=1}\langle\gamma|{}^i\mathbf{r}_j{}^2|\gamma\rangle,$$

the values of η should be between 1.0 and 0.1. The value of $(\mathbf{r}_i)^2$ increases with decreasing lattice energy because a smaller perturbing potential in the crystal influences the electronic orbits of an ion less, and therefore, the perturbation effects occur further away from the nucleus. Consequently, η increases when $E_c{}^t$ decreases, and vice versa, so that the product of these two quantities should vary little over the range of lattice energies in the alkali halides.

We estimate the average value of η in the following manner. The perturbation of the electron density associated with an outer orbital is assumed to take place beyond the outer point of inflection in the radial electron-density function. The average value of $\mathbf{r}_i^0$ is taken to be that point on the r axis where the electron-density function would intersect if it continued linearly from the point of inflection with the slope at that point. In order to evaluate these quantities, we make use of the electronic orbitals of the form proposed by Slater.[18] The result is

$$\eta \approx \frac{[(n^*)^2/(z-s)]^2[1+(1/2n^*)^{1/2}]^4}{8(n^*)^2(n^*+1)(n^*+\frac{1}{2})/(z-s)^2} = \frac{(n^*)^2[1+(1/2n^*)^{1/2}]^4}{8(n^*+1)(n^*+\frac{1}{2})}. \tag{36}$$

Here we have assumed that only the outer eight orbitals contribute appreciably to the diamagnetic susceptibility. The values of η obtained from (36) vary between 0.34 for $n^*=2$ and 0.31 for $n^*=4$, which, according to Slater's rules, correspond to the principal quantum numbers $n=2$ and $n=5$, respectively. The case $n=1$ is not included, since the Li ion does not contribute appreciably to the susceptibilities of the lithium halides. The $n=5$ value is the maximum quantum number which need be considered for the alkali halides.

Because the mean excitation energies vary in nearly the same manner the quantity β, which is a ratio of $\bar{E}$'s, should remain virtually constant and near unity in value for all the alkali halides. This means that since ηE_c^t varies little for the alkali halides and $\bar{E}_v$ remains virtually constant, the quantity $\eta\beta E_c^t/\bar{E}_v$ should also be virtually constant for all these materials, in accord with the observation made in the last section. We can now make a quantitative estimate of the value of this quantity in the alkali halides by using the value $\beta=1$, and the median values for $E_c^t/\bar{E}_v$ and η of 0.26 and 0.33, respectively, to obtain the result $\eta\beta E_c^t/\bar{E}_v \approx 0.09$. This numerical value agrees favorably with the value 0.11 obtained in the last section.

The results of the last section and the above theoretical calculation agree on the approximate validity of the relation $\chi_{\text{para}}=-0.11\chi_{\text{dia}}$ for the alkali halides. According to (26), this conclusion means that for these crystals, $(2\beta/3)\langle\lambda_i(\lambda_i+1)\rangle_{\text{av}}=0.11$, and furthermore that if β is essentially constant for all of these materials, $\langle\gamma|\mathbf{L}_1^2|\gamma\rangle$ must also be. In this sense, the average deformation per electronic orbit is the same in all of these materials.

Because the above numerical estimate is quite crude, a more important test of the theory lies in its application to other ionic crystals. A natural set of materials to study in this connection is the alkaline-earth oxides. These materials have the NaCl structure (with the exception of BeO) and otherwise are similar to the alkali halides in many respects. In applying (35) to these materials, we would expect that $\eta\beta/\bar{E}_v$ behaves in a manner similar to its behavior in the alkali halides, i.e., increases with decreasing lattice energy, but otherwise has roughly the same range of values. From this we conclude that the dominant factor in determining the ratio $\chi_{\text{para}}/\chi_{\text{dia}}$ for this series of compounds is the average magnitude of the lattice energy per ion.

TABLE III. Calculated diamagnetic susceptibilities and observed susceptibilities for the alkaline earth oxides in 10^{-6} emu/mole. The number of electrons per molecule is n_1+n_2 and the molar electric polarizability is α_M.

	n_1+n_2	α_M (Å^3)	$\lvert\chi_{\text{dia}}\rvert_{\text{calc}}$	$\lvert\chi_{\text{dia}}\rvert_{\text{calc}}^{\text{corr}}$	$\lvert\chi_{\text{obs}}\rvert$	χ_{para}
MgO	20	1.74	18.2	20.0	10.2	9.8
CaO	28	2.84	27.5	31.5	15	16.5
SrO	46	3.44	38.8	39.5	35	4.5
BaO	64	4.56	52.8	52.0	29.1	22.5

Table III lists the relevant magnetic data for testing this conclusion. The values of α_M and $|\chi_{\text{obs}}|$ were again taken from Refs. 5 and 15, respectively, while $|\chi_{\text{dia}}|_{\text{calc}}$ was again calculated by means of Eq. (5). The correction of Eq. (5) was made by assuming, in accord with the observations made earlier with regard to the alkali halides, that $|\chi_{\text{dia}}|\times 10^6/n$ has a magnitude of approximately unity for each of the ions. $|\chi_{\text{dia}}|_{\text{calc}}^{\text{corr}}$ was then obtained from $|\chi_{\text{dia}}|_{\text{calc}}$ by multiplication by the factor $[1+(n_aK_a+n_cK_c)/(n_a+n_c)]$. When used in the alkali halides, this correction procedure reproduced the more complicated procedure described in the last section to within a fraction of a percent in most cases with none of the results differing by more than about $2\frac{1}{2}\%$.

The lattice energies of the alkaline-earth oxides are on the average about five times as large as those of the alkali halides. If our theoretical conclusions are correct, then $\chi_{\text{para}} \approx 0.5|\chi_{\text{dia}}|$ for these crystals. In Table III, we see that this is indeed the case with the single exception of SrO, where the paramagnetic susceptibility is much smaller than expected. This exception may well be due to an inaccuracy in the observed susceptibility, since it is unlikely that SrO differs appreciably in its properties from those of the other compounds in the sequence.

It is apparent, then, that the factor which determines the ratio $\chi_{\text{para}}/\chi_{\text{dia}}$ for an ionic crystal is E_c^t/t, or the average lattice energy per ion. If the lattice energy per ion is large enough, the crystal displays a paramagnetic susceptibility. This is apparently the case in some of the transition-metal oxides, which have a large average lattice energy per ion because of the large valences of the constituent ions. We will consider one such example in numerical detail here, namely, that of rutile, about which a considerable amount of information is available. The lattice energy of rutile, as determined by means of the Born-Haber cycle is about 2900 kcal/mole, which is about ten times the lattice energy per ion calculated for the alkali halides. According to the above theory, this should result in a slightly paramagnetic crystal, in accord with the observed result.[8]

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[18] J. C. Slater, Phys. Rev. 36, 57 (1930).

IV. ANALYSIS OF RESULTS AND CONCLUSIONS

In this work, we have presented what appears to be the first determination and theoretical analysis of the paramagnetic susceptibilities of ionic crystals. The trend of the paramagnetic susceptibilities of the alkali halides was first determined in a semiempirical fashion by comparing calculated diamagnetic susceptibilities with the observed susceptibilities. This trend suggested a theoretical analysis which predicted, in addition, that the paramagnetic susceptibilities of ionic crystals with larger lattice energies per ion should be proportionately larger. This prediction was shown to be fulfilled in the alkaline-earth oxides, and indicated, in addition, the reason for the observed paramagnetism in certain transition-metal oxide crystals.

We are now in a position to analyze critically the assumptions and conceptual foundations underlying the theory. First, it is apparent from the results that if the contention had not been made initially that the angular kinetic energies of the crystalline systems considered equal E_c in magnitude, then it would have been necessary to assume that the angular kinetic energy equals a substantial and virtually constant proportion of the total kinetic energy of crystallization in the materials considered. Otherwise, the theory cannot be made consistent with experimental results. Consequently, the contention is consistent with experiment.

Of greater importance, however, is the examination of the basic mechanism which was assumed in arriving at this contention, namely, the dominance of the point charge potential in producing the effect. The significant issue here is whether the effect takes place beyond the nearest-neighbor distance, as would be required by the point-charge model. This issue can be settled by simple calculation, taking advantage of some of the results of the previous section.

Using the median value of 0.26 for $E_c^t/\bar{E}_v$ and assuming β to be unity, one finds that the quantity η must on the average equal about 0.42 in order that the theory conform to experimental observation. Next, using the value $\bar{E}_v = 32$ eV arrived at in the last section, and taking $N=36$ as a typical value for the number of electrons in an ion, one finds, making use of the above result, that $\mathbf{r}_i^0$ is equal to about 2.4 Å. This value, however, is probably too small since the quantity $\beta = \bar{E}_v^2/\bar{E}_2\bar{E}_M$ would be expected to be less than unity for two reasons. First, since the sum which defines $\bar{E}_v$ does not contain a negative correlation term, while that defining $\bar{E}_2$ does, $\bar{E}_v$ is necessarily smaller than $\bar{E}_2$ (see Appendix I). Second, in the only case where the quantities $\bar{E}_2$ and $\bar{E}_M$ are known, namely in the case of the hydrogen atom, $\bar{E}_M$ is about 35% larger than $\bar{E}_2$.[7] If this is a typical result, and the quantity β is typically some 35 to 40% smaller than unity, then a typical value for $\mathbf{r}_i^0$ is 2.7 to 2.8 Å, a distance representative of the nearest-neighbor separations in the alkali halides, and somewhat larger than those in the alkaline-earth oxides.

We see, then, that these calculations support the contention that the ionic perturbations take place beyond the nearest-neighbor distance. This, in turn, lends support to the reasonableness of the point-charge model. In fact, since the theory indicates that the perturbations which produce the paramagnetism (and presumably the changes in ionic polarizabilities and diamagnetic susceptibilities as well) take place at such large distances from the nucleus, it would be difficult to think of any other mechanism which would produce such an effect. This idea gains further support when one realizes that the assumption that the angular kinetic energy is a fraction of E_c less than unity necessarily requires that $\mathbf{r}_i^0$ be *larger* than the values determined above. Of course, further support of this idea must await more theoretical work and comparison with experimental data.

One of the basic conclusions which may be derived from this work is that the crystalline paramagnetism, which is the result of the nonspherical ionic deformations, is a necessary part of the chemical binding process. In this connection, the manifestation of a paramagnetic susceptibility in a crystal is not a contradiction of the ionic model. On the contrary, the results of this work suggest that in an isoatomic sequence of ionic compounds, the paramagnetic susceptibility should very nearly be a constant percentage of the observed susceptibility. This indicates that the magnetic data could be used as a tool in the analysis of bond types in crystals. Therefore, it is hoped that this work will provide an impetus for the accumulation of more extensive and accurate magnetic data of crystals, and the means for their analysis.

APPENDIX A: THE NONADDITIVITY OF THE IONIC DIAMAGNETIC SUSCEPTIBILITIES

The changes in the diamagnetic susceptibilities of free ions when they are transported into the crystalline environment may be discussed in a manner which parallels the analysis of the ionic polarizabilities in Ref. 7. In that work, the Thomas-Kuhn-Reiche sum rule was written in the form

$$\bar{E}_2 \sum_{\gamma'} |\langle\gamma|\mathbf{R}|\gamma'\rangle|^2 = \bar{E}_2\langle\gamma|\mathbf{R}^2|\gamma\rangle = 3\hbar^2 N/2m, \quad \text{(A1)}$$

where $\mathbf{R} = \sum_{i=1}^N \mathbf{r}_i$, $\mathbf{r}_i$ is the radius vector of the ith electron, and N is the total number of electrons. This relation was then used to express the electronic polarizability in the form

$$\alpha = \frac{e^2 N\hbar^2}{m\bar{E}_2\bar{E}_3} = \frac{e^2 N\hbar^2}{m\bar{E}_1^2}. \quad \text{(A2)}$$

The mean excitation energies $\bar{E}_1$, $\bar{E}_2$, and $\bar{E}_3$, while not identical, generally have numerical values which are close to each other. Within the framework of the product approximation for ionic crystals discussed in Ref. 7, Eq. (A2) was then applied to the individual ions. Quantitative estimates of the decreases in the values of the $\bar{E}_1$'s for the cations and increases in the values of $\bar{E}_1$'s for the anions in the alkali halides brought about by the influence of the Madelung potential were made. From these were obtained, using Eq. (A2), quantitative values for the electronic polarizabilities of the ions in the alkali halides which agreed favorably with the least-squares values. The corresponding increase and decrease in the cation and anion ionic radii was also inferred from this analysis.

An analysis similar to this can be used for the ionic diamagnetic susceptibilities. Within the framework of the product approximation, the diamagnetic susceptibility of an ionic crystal exhibiting over-all inversion symmetry, i.e., $\langle\gamma|\mathbf{R}|\gamma\rangle=N\langle\gamma|\mathbf{r}_1|\gamma\rangle=0$, can be written in the form[8,19]

$$\chi_{\text{dia}}=\sum_{i=1}^{M}\chi_{i\,\text{dia}}=\frac{e^2}{6mc^2}\sum_{i=1}^{M}\sum_{j=1}^{ni}\langle\gamma|{}^i\mathbf{r}_j{}^2|\gamma\rangle\,, \tag{A3}$$

where η_i is the number of electrons associated with the ith electron group, and M is the number of ionic electron groups. We can now make use of the sum rule[17]

$$\sum_{i=1}^{N}\sum_{\gamma'}(E_{\gamma'}-E_{\gamma})|\langle\gamma|\mathbf{r}_i|\gamma\rangle|^2=3\hbar^2N/2m\,. \tag{A4}$$

This sum rule is similar to the Thomas-Kuhn-Reiche sum rule, and differs in that it does not contain the correlation term

$$\sigma=\sum_{i=1}^{N}\sum_{j=1}^{N}{}'\langle\gamma|\mathbf{r}_i\cdot\mathbf{r}_j|\gamma\rangle$$

in the sum. If we define a mean excitation energy $\bar{E}_v$ such that

$$\bar{E}_v\sum_{i=1}^{N}\sum_{\gamma'}|\langle\gamma|\mathbf{r}_i|\gamma'\rangle|^2$$
$$=\bar{E}_v\sum_{i=1}^{M}\sum_{j=1}^{ni}\langle\gamma|{}^i\mathbf{r}_j{}^2|\gamma\rangle=3\hbar^2N/2m\,, \tag{A5}$$

then χ_{dia} can be written in the form

$$\bar{E}_v(6mc^2/e^2)\chi_{\text{dia}}=3\hbar^2N/2m\,, \tag{A6}$$

and an inverse proportionality exists between χ_{dia} and $\bar{E}_v$.

The apparent ease with which we have bypassed the problem of evaluating the quantity σ which appears in the Thomas-Kuhn-Reichesum rule is misleading since we have actually substituted one problem for another. As has already been explained,[17] the sum rule (A4) does not involve observable transitions, but rather, unobservable one-particle transitions. Consequently, the excited states involved in the sum can include the unobservable symmetric states and states of mixed symmetry in addition to the observable antisymmetric states. Therefore, $\bar{E}_v$ is a weighted average energy of excitation which involves the energies of all the eigenstates of the Hamiltonian and not just the observable excited states as is the case for the quantity $\bar{E}_2$.

The value of the sum rule (A4) lies in the fact that in many cases, it is much easier to estimate the relationship between $\bar{E}_v$ which appears in (A5) and the $\bar{E}$'s which result from sum rules involving real transitions than to determine the magnitude of σ and its variations directly. In this particular case, it is demonstrated in Appendix B that the ratio $\bar{E}_2/\bar{E}_v$ for the free-ion system is very nearly the same as that for the crystalline system. This means that the discussion given in Ref. 7 in which quantitative values for the electronic polarizabilities of ions in the alkali halides are obtained is also applicable to the diamagnetic susceptibilities of the ions. However, because χ_{dia} is inversely proportional to a mean excitation energy rather than its square, as is the case for α, the percent change in the diamagnetic susceptibility of an ion when it is transported into the crystal is roughly half that of the electronic polarizability.

APPENDIX B: THE RELATIONSHIP BETWEEN $\bar{E}_2$ AND $\bar{E}_v$

In this section, we wish to establish the connection between the quantity $\bar{E}_2$ obtained from the Thomas-Kuhn-Reiche sum rule and the quantity $\bar{E}_v$ obtained from the sum rule for one-particle transitions (A4). In particular, we wish to establish that the relative changes in these two quantities when the free-ion system undergoes crystallization are essentially the same.

The Thomas-Kuhn-Reiche sum rule involves transition integrals of the type

$$\langle\gamma|\mathbf{R}|\gamma'\rangle=\int\Psi_{\gamma}\mathbf{R}\Psi_{\gamma}{}'d\tau\,, \tag{B1}$$

while the sum rule (A4) involves the transition integrals

$$\langle\gamma|\mathbf{r}_i|\gamma'\rangle=\int\Psi_{\gamma}\mathbf{r}_i\Psi_{\gamma}{}'d\tau\,. \tag{B2}$$

Since $\mathbf{R}$ is completely symmetric in all the particles of the system, the $\Psi_{\gamma'}$ in (B1) must all be antisymmetric functions of the particle indices, just as is the ground-state wave function Ψ_{γ}. This prohibition does not apply to (B2) so that the Ψ_{γ}, which appear in these integrals include the unobservable states as well. Since $\langle\gamma|\mathbf{R}|\gamma'\rangle=N\langle\gamma|\mathbf{r}_i|\gamma'\rangle$ when the $\Psi_{\gamma'}$ are restricted to the observable states, our problem consists of evaluating the contribution to the sum (A4) of the transition integrals in which the unobservable $\Psi_{\gamma'}$ appear. In

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[19] The superscript i was not used in Ref. 8 but is included here to make clearer the summation over electron groups.

order to do this, we will separate the unobservable $\mathbf{\Psi}_{\gamma'}$ into two classes, those in which two or more electrons have the same spin and/or orbital quantum numbers, and those which do not. The first will be shown to make an unimportant contribution to the sum (A4), while the terms involving the latter will be shown to behave in essentially the same way as those involving the observable $\mathbf{\Psi}_{\gamma'}$.

The argument can be summarized as follows: First, we consider the system of free ions. The antisymmetric ground state of each ion is a spherically symmetric, spinless state. We imagine a complete set of functions from which a set of electronic spin orbitals can be constructed. All of the observable ionic states can be constructed from expansions of Slater determinants of the spin orbitals. The unobservable ionic states are not antisymmetric and must, therefore, be constructed from series expansions involving permanents of the spin orbitals, in the case of completely symmetric states, or expansions involving products of permanents and determinants of the spin orbitals, in the case of states of mixed symmetry. Now any one-particle-transition integral involving an observable and an unobservable state which has two or more electrons in the same orbital will generally vanish since at least two orbitals will usually be paired in the integrand which have either different spins and/or orbital angular momenta. In either case, the orbitals are orthogonal, and the integral vanishes. Possible nonvanishing contributions exist in transitions which involve highly ionized excited states in which several electrons are stripped away from the ion core. However, these states are energetically far removed from the ground state in comparison with the values of $\bar{E}_v$ determined earlier, so that we may conclude that the terms involving these states do not contribute appreciably to the sum (A4). When the ions form the crystal, the electronic orbitals acquire an additional component, which to first order, has the point symmetry of the crystalline environment surrounding the ion. The orthogonality of the orbitals discussed above does not apply to these added components, but since the crystal is assumed to have overall inversion symmetry, the transition integral will still vanish, since the orbitals have the inversion symmetry, while the total integrand does not.

The only appreciable contributions to the sum (A4) which involve unobservable states are those in which the unobservable states do not contain orbitals in which quantum numbers are duplicated. These unobservable states differ energetically from the observable states primarily in the expectation values which they yield for the two-electron interaction potential

$$V_{ij}=\sum\nolimits_{i\neq j} e^2/r_{ij}$$

which appears in the nonrelativistic Hamiltonian. This energy difference is relatively small and is of the order of the exchange energy which appears in the Hartree-Fock treatment. A completely symmetric function includes no exchange, while a function of mixed symmetry includes some since such a function is antisymmetric in some of its electron indices. The expectation value of V_{ij} should not vary much because of the crystallization process, since the percent change in the total energy of the system in this process is small. Therefore the unobservable excited states of this type shift with respect to the ground state in essentially the same manner as do the observable excited states. The lowest-lying unobservable state does not contribute to the sum (A4) since, like the observable ground state, it has inversion symmetry both in the free-ion system and in the crystal. Consequently $\langle\gamma|\mathbf{r}_i|\gamma'\rangle$ vanishes in this case. This means, then, that in the passage from the free ion to the crystalline system, the unobservable states which contribute in any appreciable manner to the sum (A4), and consequently to $\bar{E}_{v'}$ shift in essentially the same manner with respect to the ground state as do the observable states which determine the change in $\bar{E}_{2'}$ so that $\bar{E}_2$ and $\bar{E}_v$ maintain an almost constant proportionality.

The meaning of this conclusion can be seen by comparison of Eqs. (A1) and (A5). If the quantities $\bar{E}_v$ and $\bar{E}_2$ remain strictly proportional, then this means that the ratio of

$$\sigma=\sum_{i=j}\langle\gamma|\mathbf{r}_i\cdot\mathbf{r}_j|\gamma\rangle \quad\text{and}\quad \sum_i\langle\gamma|\mathbf{r}_i{}^2|\gamma\rangle$$

must also remain constant. Now if we set $\langle\gamma|\mathbf{r}_1\cdot\mathbf{r}_2|\gamma\rangle=\langle\gamma|\mathbf{r}_1{}^2|\gamma\rangle\cos\boldsymbol{\eta}$, where the "correlation angle" $\boldsymbol{\eta}$ is the average angle between the two electronic radius vectors, this results means that $\cos\boldsymbol{\eta}$ has essentially the same value for both the free ion and crystalline systems. This conclusion is in accord with the calculations by Hart and Herzberg[20] on the mass polarization correction to the energy of the helium atom. Their results indicate that $\langle\gamma|\mathbf{p}_1\cdot\mathbf{p}_2|\gamma\rangle$ for the ground state increases roughly as the square root of the total energy. Since $\langle\gamma|\mathbf{p}_1{}^2|\gamma\rangle$ is proportional to the total electronic energy by the virial theorem, this means that in this case $\cos\boldsymbol{\eta}$ decreases roughly as the square root of the total energy. Since the crystalline system has a total electronic energy of only a small fraction of a percent less than that of the free-ion system, the calculations for the helium atom support the above conclusion that $\cos\boldsymbol{\eta}$ remains essentially constant in the transition from the free ion to the crystalline system. In a similar manner, this conclusion also is substantiated in the case of the individual ions, since the magnitude of the crystalline potential is usually no more than a few percent of the total energy of a given ion.

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[20] J. Hart and G. Herzberg, Phys. Rev. **106**, 79 (1957).