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Calculation of the Crystalline Field Strength: Chrome Alum

A. J. FREEMAN
Materials Research Laboratory, Ordnance Materials Research Office, Watertown, Massachusetts, and Solid State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts

AND

R. E. WATSON*†
Solid State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts

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A calculation of the crystalline field strength, *Dq*, is reported for the case of chrome alum, using the same model and crystal field potential employed by Kleiner and recently determined Hartree-Fock wave functions for the Cr^{+3} ion. On this basis, earlier theoretical attempts at determining, within the framework of crystal field theory, accurate *Dq* values are reviewed and analyzed. Particular emphasis is placed on a consideration of reported point charge calculations and Phillips' method of including the effects of orthogonalization of ligand to metal ion wave functions. Our results indicate that the point charge model estimates for *Dq* gave good results mostly because they were based on the use of improper *3d* wave functions for the transition metal cation. Kleiner's result is significantly improved—his wrong sign for *Dq* is reversed and a small positive *Dq* is obtained—but in such a way as to contradict Phillips conclusions. A discussion is given of the various evidence for the inadequacy of the electrostatic potential theory and some of the necessary modifications are indicated.

1. INTRODUCTION

It is by now well known that the Bethe[1] and Van Vleck[2] crystal field theory has on the whole had a striking success throughout its long history in interpreting a wide range of experimental data.[3–7] Most recently it has found wide use and acceptance in analyzing optical absorption and paramagnetic resonance experiments.[4,7] In order to achieve this success,[8] however, the strength of the crystalline field, usually represented by *Dq* and unevaluated in the theory, is left as a parameter to be determined empirically.

Despite these successes, crystal field theory has never been theoretically justified in that, although in principle *Dq* can be determined theoretically within the framework of the theory, no accurate *a priori* determinations of the crystal field strength have in fact been made. Attempts at estimating *Dq* have been made by Van Vleck,[9] Polder,[10] and others, with apparent success, employing a crude point charge or point dipole model to represent the electrostatic field arising from the ligand atoms. Based on these estimates, much has since been made in the literature of their result as seemingly placing crystal field theory on a firm foundation, even though Van Vleck himself suggested that the good agreement was perhaps accidental. More recently Kleiner[11] attempted to check the theory in more detail by calculating the crystalline field strength on the basis of a more refined model for the charge distribution of the ligand atoms. As his particular case he chose that of the Cr^{+++} ion in chrome alum, which had also been treated earlier by Van Vleck.[9] Kleiner's result, which was obtained after a good deal of elaborate calculation, gave a value for *Dq* of the wrong sign. This he associated with the large negative contribution of the overlap of charge between the Cr^{+++} and O^{--} charge densities. Kleiner concluded that the interaction between the Cr^{+++} and the ligand ions was so strong that the crystalline field approximation was inadequate for giving detailed agreement between theory and experiment.

The attempt of Tanabe and Sugano[12] to correct Kleiner's calculation by including the effect of the overlapping charges in a modified molecular type calculation resulted in a failure of the opposite sort. These authors found a *Dq* of the proper sign but of a magnitude incorrect by a factor of two. Their calculation does not follow from the electrostatic model as direct interactions (Coulomb and exchange) are allowed between metal ion and ligand orbitals. Since the calculations were quite involved, many approximations and extrapolations were necessary and it is not clear how these affected the final results.

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* The research done by this author was supported jointly by the U. S. Army, Navy, and Air Force under contract with the Massachusetts Institute of Technology.

† Now at Avco, RAD, Wilmington, Massachusetts.

[1] H. Bethe, Ann. Physik **3**, 133 (1929).

[2] J. H. Van Vleck, Phys. Rev. **41**, 208 (1932).

[3] The many references to this work are too numerous to list. Instead the reader is referred to the review articles listed in references 4–7.

[4] B. Bleaney and K. W. H. Stevens, *Reports on Progress in Physics* (The Physical Society, London, 1953), Vol. 16 p. 108; K. D. Bowers and J. Owen, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. 18, p. 304.

[5] D. S. McClure in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1959), Vol. 9, p. 399.

[6] W. E. Moffitt and C. J. Ballhausen, Ann. Rev. Phys. Chem. **7**, 107 (1956).

[7] W. Low, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1960), Suppl. 2.

[8] Recent evidences have indicated that discrepancies exist; there will be discussed in Sec. 4.

[9] J. H. Van Vleck, J. Chem. Phys. **7**, 72 (1939).

[10] D. Polder, Physica **9**, 709 (1942).

[11] W. H. Kleiner, J. Chem. Phys. **20**, 1784 (1952).

[12] Y. Tanabe and S. Sugano, J. Phys. Soc. (Japan) **11**, 864 (1956).

Phillips[13] has published an apparent justification for the suggestion by Slater, Herring,[14] and others, that Kleiner's negative result arose from the neglect of orthogonalization terms between the Cr^{+++} and O^{--} functions. He showed that to a first approximation all the effects due to the extension of the ligand charge distribution (such as overlap and orthogonalization) cancel and that apparently the usual estimates based on the point ions approach, which gave good values for the crystal field splittings, are indeed well justified.

It is our purpose to further explore these questions in some detail, basing our calculations on recently computed[15] Hartree-Fock solutions for the free Cr^{+++} ion. Since the molecular orbital treatment of Tanabe and Sugano is not conveniently related to conventional crystal field theory while the approach of Phillips is, discussion will be most heavily related to the latter in what follows.

Our work centers on the calculation of the crystalline field strength for chrome alum using the same model and crystal field potential employed by Kleiner.[16] On this basis the earlier point charge calculations are discussed and Phillips' method is reviewed and analyzed. Our results indicate that the point charge model estimates for Dq gave good results because they were based on the use of hydrogenic $3d$ wave functions for the transition metal cation. Further, Kleiner's result is significantly improved—his wrong sign is reversed and a small positive Dq is obtained—but in such a way as to contradict Phillips' conclusions.

2. CALCULATION OF THE CRYSTALLINE FIELD STRENGTH: CHROME ALUM

In the crystalline field theory of Bethe[1] and Van Vleck,[2] the $3d$ electrons of the central ion in a crystalline environment are considered as being under the influence of the electrostatic field due to the nuclear charges and an average electron distribution of ligands. No consideration is included of allowing for any modification of the electron orbits, from their free-ion values,[17] despite the fact that the overlap of metal and ligand charge densities is not negligible. Kleiner's calculation is strictly based on what may be called the naive crystal field approach.

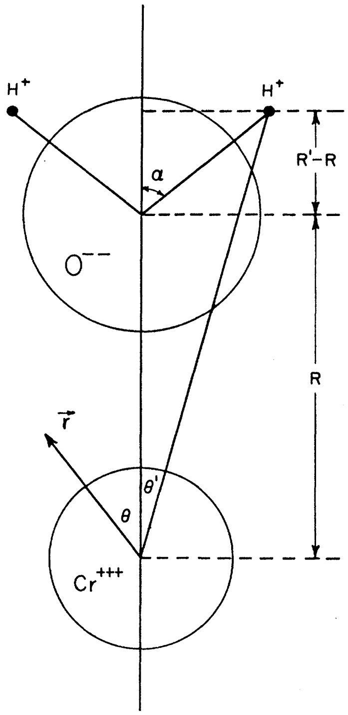

FIG. 1. Nuclear configuration for the Kleiner model of Cr^{+++} and a H_2O molecule in chrome alum. The calculations discussed in the text are for several values of R', R, and α.

A. Outline of the Calculations

In what follows we employ essentially the same model, crystal field potential, and methods used by Kleiner in his discussions.[11,16] The quantity we wish to calculate is Dq which is given as

$$Dq=(14\pi^{\frac{1}{2}})^{-1}\int_0^\infty P_{3d}^2(r)V_4(r)dr, \tag{1}$$

where $r^{-1}P_{3d}(r)$ is a normalized $3d$ radial wave function for Cr^{+++} and $V_4(r)$ is the radial component of the $l=4$ term of the crystal field potential expanded in the usual form as a series of products of radial functions and spherical harmonics of order l having cubic symmetry.

The model of $Cr^{+++}\cdot 6H_2O$ as chosen by Kleiner (and followed by Tanabe and Sugano as well) is that of 6 water molecules octahedrally coordinated about a central Cr^{+++} ion; each water molecule is assumed to consist of a spherically symmetrical O^{--} ion with its center located on a coordinate axis a distance R from the origin and two hydrogens which are situated as shown in Fig. 1 but which are represented as a ring of charge about the $Cr^{+++}-H_2O$ axis (this in order to preserve cubic symmetry). $R'-R$, the distance of the plane of the ring from the O^{--} center, determines the dipole moment of the H_2O molecules; changing α also affects the dipole moment and this contributes to a change in Dq as well.

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[13] J. C. Phillips, J. Phys. Chem. Solids **11**, 226 (1959).

[14] C. Herring, in *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4–6, 1954*), edited by R. G. Breckenridge *et al.* (John Wiley & Sons, Inc., New York, 1956).

[15] R. E. Watson, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology Technical Report No. 12, 1959 (unpublished).

[16] W. H. Kleiner, PhD thesis, Physics Department, Massachusetts Institute of Technology, 1952 (unpublished), contains extensive information on a wide range of calculations carried out as part of this author's investigations. Only a small portion of this work is given in reference 11. We have retained Kleiner's notation except for the substitution of the more common Dq for his Q; $10Dq$ is the cubic field energy difference of the triply and doubly degenerate $3d$ orbitals.

[17] In addition, the constraints associated with the conventional Hartree-Fock formalism are also assumed. For a discussion of some effects on free-ion wave functions arising from the relaxation of these constraints, see R. E. Watson and A. J. Freeman, Phys. Rev. **120**, 1125 (1960).

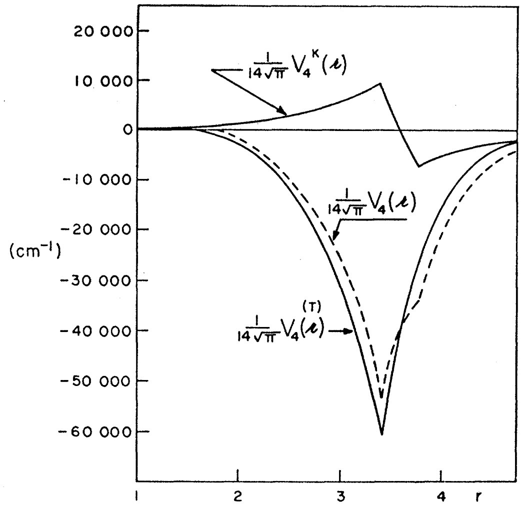

FIG. 2. The separate contributions to $V_4(r)$, the $l=4$ term of the crystal field potential; $V_4(r)$ is the contribution from the finite dipoles; and $V_4^T(r)$ is a contribution from a "correction" charge or overlap term due to the extension of the O^{--} charge density (as considered by Kleiner[16]).

From the model just discussed $V_4(r)$ was determined by Kleiner to consist of essentially two terms which contribute to Dq: (a) a contribution from finite dipoles, called by him $V_4^K(r)$, and (b) a contribution from a "correction" charge or overlap term due to the extension of the O^{--} charge density and called $V_4^T(r)$. These separate contributions to $V_4(r)$ are shown in Fig. 2 as is $V_4(r)$. (For simplicity a very small overlap contribution due to the $O^{--}1s$ electrons has been left out of the figure, and our calculations as well.)

Although he carried out careful calculations for a whole range of values of the parameters R', R, and α,[16] in his paper[11] Kleiner discussed only that model of the nuclear configuration which involved those values of the parameters which gave the best possible value of Dq. [In this way he was able to emphasize that his negative result did not depend on a particular (and perhaps poor) choice of the parameters in question.] This necessitated using a dipole moment for the H_2O molecule which was *three times* as large as the free molecule moment of 1.86×10^{-18} esu, the increase presumably arising from the polarization of the waters by the Cr^{+++} ion.[18] While this large a polarization is perhaps difficult to accept, experimental data which would confirm or refute this conjecture are lacking at present. Nevertheless, we emphasize this assumption here as it plays a large role in any interpretation of the results.

There next remains the choice of wave function with which to evaluate the integrals in Eq. (1). Kleiner (and Tanabe and Sugano) used the Hartree[19] SCF solution without exchange for Cr^{++} since no Hartree-Fock wave functions were then available. For comparison we show in Fig. 3 Watson's[15] Hartree-Fock $3d$ wave function for Cr^{+++} along with the Hartree Cr^{++} wave function and the hydrogenic $3d$ wave function used by Van Vleck[9] in his early point charge calculation. We see that the functions are quite different and that this difference is one of shape rather than scaling. It is clear from this figure and Fig. 2 that the different wave functions each emphasize a different region of $V_4(r)$ and that quite different results are to be expected from each of them. In fact, Van Vleck's[9] and Polder's[10] point charge calculations give such good agreement with experiment for just this reason—namely, that their hydrogenic $3d$ functions are so greatly expanded (see Fig. 3) with respect to SCF wave functions as to give a very much larger contribution to Dq.[20] Furthermore, Van Vleck didn't use a point charge potential of the form shown in Fig. 2 for $V_4^K(R)$ (which shows a change in form at $r=R$) but instead defined Dq by

$$Dq=\frac{2}{105}D\int_0^\infty P_{3d}^2(r)r^4dr, \tag{2}$$

where D is a constant equal to $-35ee_{\text{eff}}/4R^5$ and e_{eff} is an effective charge (set equal to $-1.01e$ in Van Vleck's calculation). This form of the potential also increases the calculated value of Dq.

While the question of what the "real" $3d$ radial function looks like remains unresolved, crystal field theory in its formulation calls for the use of the best free atom wave function. On this basis then, the Hartree-Fock Cr^{+++} $3d$ function is required. This latter function is

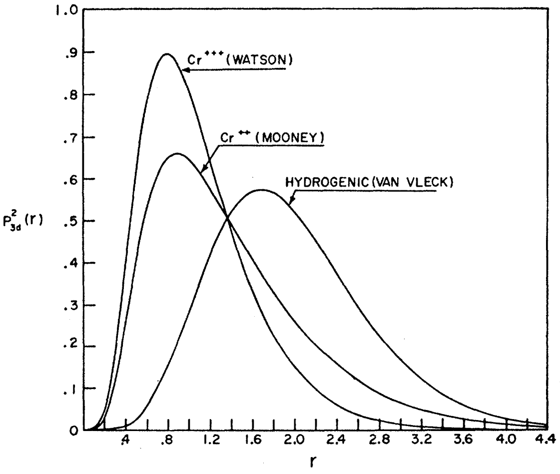

FIG. 3. Watson's Hartree-Fock $3d$ wave function for Cr^{+++}; Mooney's Cr^{++} $3d$ wave function (without exchange) and the hydrogenic $3d$ function used by Van Vleck.

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[18] In his calculation Van Vleck[9] estimated the dipole moment to be 1.92×10^{-18} esu, in good agreement with the free molecule value, and assuming a point dipole model he obtained a value for Dq close to the experimental one.

[19] R. L. Mooney, Phys. Rev. **55**, 557 (1939).

[20] We are grateful to W. Marshall for first emphasizing this point to us and for several discussions.

used in the present calculations, leaving such effects as orthogonalization and covalency to be discussed in later sections.

B. Results

Kleiner used an analytic expression fitted to the Cr^{++} $3d$ wave function and was therefore able to evaluate analytically the integrals pertinent to Eq. (1). Since the potential $V_4{}^T(r)$ was available to us in numerical form our computations were more easily performed using numerical methods. As a check on any possible differences between the methods of computation, we have repeated Kleiner's calculations only with the Cr^{++} wave functions retained in numerical form; the results agree except for small unimportant differences.

Following Kleiner,[16] our results are best summarized by plotting the separate contributions to Dq as a function of the parameters R', R, and α. See Fig. 4. $K(R',R)$ and $T(R)$ are the contributions to Dq from the point dipoles and overlap of charge, respectively. The solid curves are Kleiner's data and the dashed curves are our results for the same quantities (as indicated by the primes). K is the dipolar contribution for a dipole moment corresponding to the free water molecule value (hence $R'-R=0.37$ atomic units) with the two protons represented as a point charge $2e$ on the $Cr^{+++}-O^{--}$ axis ($\alpha=0$ in Fig. 1), whereas K_1 and K_2 are the dipolar contributions corresponding to two alterations of the water molecule in the $Cr\cdot 6H_2O^{+++}$ complex which Kleiner considered. K_1 corresponds to increasing the dipole moment of the water molecule by moving the point charge $2e$ out along the $Cr^{+++}-O^{--}$ axis such that $R'-R$ is changed from 0.37 to 1.10, thus increasing the dipole moment threefold from the free water molecule value and thereby increasing Dq. K_2 corresponds to the triangular model for H_2O shown in Fig. 1 with the hydrogens represented by a cylindrically averaged charge distribution. This procedure diminishes the effect of the protons and increases both the dipolar contribution and Dq. Kleiner's published results[11] were for this model (with $2\alpha=105°$)—clearly the most favorable one consistent with an assumed $Cr^{+++}-O^{--}$ distance, R, equal to 3.73 a. u. (the H_2O-Al^{+++} distance observed in aluminum alum). Nevertheless, as pointed out by Kleiner,[11] even for this case the calculated Dq (-500 cm^{-1}), which is composed of the two contributions K_2(1000 cm^{-1}) and T(-1500 cm^{-1}), is much less than the observed value[21] of 1750 cm^{-1}. It is in fact of the wrong sign. Furthermore, these results indicated that if the overlap effects were not included then the point dipole model (as found also by Van Vleck) gave agreement with experiment[22] provided the dipole moment was taken as three times that of the free water molecule. These results explain Kleiner's conclusion that the crystalline field approximation was unable to give detailed agreement between theory and experiment.

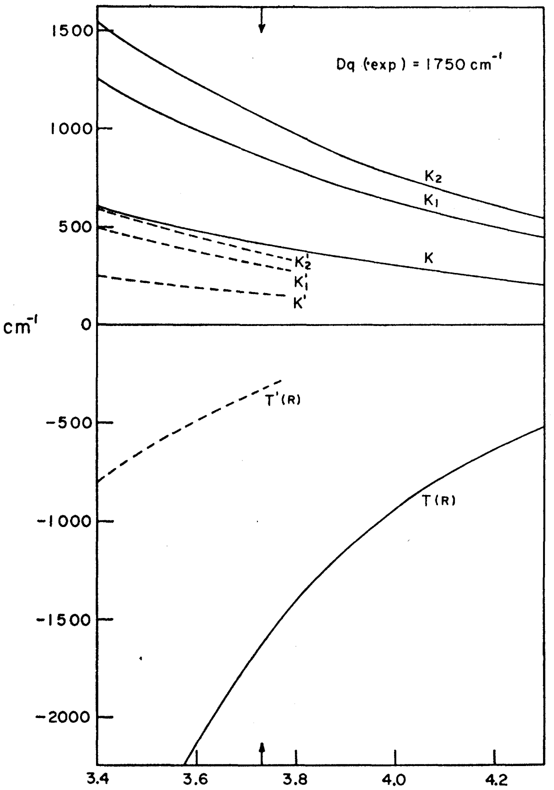

FIG. 4. $K(R',R)$ and $T(R)$ are the contributions to Dq from the point dipoles and overlap of charge, respectively. The solid curves gives Kleiner's data and the dashed are our results for the same quantities (as indicated by the primes). K, K_1, K_2 are the dipolar contributions for different values of R', R, and α (as explained in the text) and the arrows indicate the R value appropriate for the aluminum alums.

Our calculated results for these same quantities, denoted by the prime, are shown in Fig. 4 for some of the same sets of nuclear configuration parameters (while Kleiner's results[16] are for four values of R, ours rely on calculations for $R=3.4$ and 3.73 only). Comparison between the two sets of data shows some striking differences from Kleiner's results and from these some conclusions may be immediately drawn. First of all, both the dipolar and charge overlap terms are greatly reduced for all values of the parameters R', R and α once "proper" free ion Hartree-Fock wave functions are used for the Cr^{+++} ion. Second, for no choice of the parameters considered (in the range discussed) will the dipolar contribution *by itself* be large enough to lead to a Dq in agreement with experiment—not even if a dipole moment three times that of the free water molecule is used. Finally, a Dq is calculated which differs from the value calculated by Kleiner[11]; in fact for the most favorable choice of parameters the wrong sign obtained by him is reversed and a positive (but small) value of Dq is found. (Considering the various assump-

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[21] H. von Hartmann and H. L. Schlafer, Z. Naturforsch. **6a**, 760 (1951).

[22] Especially since the best estimate Kleiner had gave the range $1000 \leq Dq \leq 2000$ cm^{-1} for the experimental value of Dq.

tions invoked in order to obtain this result, no significance can be attached to this value for *Dq*.) Our result is still far from the experimental value and it therefore seems quite certain that with this model, and the inclusion of only dipolar and charge overlap terms, agreement with experiment cannot be obtained.

In the next section, we consider the question of orthogonalization as a possible way out of this dilemma.

3. THE EFFECT OF ORTHOGONALIZATION IN A CALCULATION OF THE CRYSTAL FIELD STRENGTH

It was suggested by Slater, Herring, and others, that Kleiner's poor result was to be explained as arising from the neglect of the orthogonalization terms between the Cr^{+++} ion and its ligands. (Inclusion of orthogonality terms raises enormously the complexity of the calculation and to keep the job tractable Kleiner was forced to neglect these terms.) Phillips[13] has recently attempted to include orthogonalization in a calculation of the crystal field strength. This was done using the orthogonalized plane wave method as translated by Phillips[13,23] and Quelle[24] in which the effect of orthogonalization to the ligand orbitals is included by grouping these terms into an effective repulsive potential, V_R. This is shown in the following development, which is that of Phillips.

Consider a free-ion one-electron wave function, ψ_f, which is a solution for the free-ion one-electron Hamiltonian, H_0, i.e.,

$$H_0\psi_f = E_0\psi_f. \tag{3}$$

We would like the energy for the case of this ion surrounded by a crystalline array of ions constructed from one-electron wave functions ϕ_{jlmn} (where *lmn* are the one-electron quantum numbers and *j* denotes the particular ligand ion). We could orthogonalize ψ_f to the ϕ's, obtaining

$$\psi = \psi_f + \sum_{jlmn} A_{jlmn}\phi_{jlmn}, \tag{4}$$

where

$$A_{jlmn} = -(\psi_f, \phi_{jlmn}), \tag{5}$$

the bracket denoting integration over space and spin coordinates. The energy is then obtained from the Schrödinger equation for ψ in terms of the complete crystal Hamiltonian H,

$$H\psi = E\psi, \tag{6}$$

where

$$H = H_0 + V_c; \tag{7}$$

V_c is the potential due to the surrounding ions and may be written as the sum of a point charge potential V_p and a correction for the finite size of the ions, V_L (in analogy to the radial potentials V_K and V_L, respectively, in Kleiner's notation). V_L can be made to include exchange effects. Equation (6) can be rewritten in the form

$$(H_0 + V_{\mathrm{eff}})\psi_f = E\psi_f, \tag{8}$$

where

$$V_{\mathrm{eff}} \equiv V_p + V_L + V_R, \tag{9}$$

and with V_R defined as

$$V_R \equiv \sum_{jlmn} [E - E_{nl}](\psi_f, \phi_{jlmn})\phi_{jlmn}/\psi_f. \tag{10}$$

Thus V_R is an effective repulsive potential arising from the orthogonality requirement and E_{nl} the energy obtained by applying the *total Hamiltonian H* to ϕ_{jnlm}.

This procedure has obvious merits. While departing from the standard crystalline field model, it introduces the orthogonality requirement as a one-electron potential to be added to the dipolar and overlap terms in such a way as to obtain an effective potential which resembles and replaces the usual crystal field potential, V_c. In this way, another term is formally provided with which to bring about agreement with experiment.

Having arrived at this result, Phillips then proceeded to present a general argument, based on orthogonalized plane wave calculations for silicon,[23] to show that in a calculation for *Dq*, in which the effective potential of Eq. (9) is used, the contribution of the terms V_R and V_L, which depend on the finite extension of the ligand charge distribution, should in first approximation cancel each other leaving only the dipolar term, V_P, to contribute to the field strength. Applying this conclusion to the results of Kleiner's calculation, he estimated the repulsive term to be about ten percent larger than the overlap contribution, which Kleiner had calculated to be -1500 cm^{-1} (see discussion of previous section). Thus, with V_R chosen to be 1700 ± 400 cm^{-1} (allowing for an uncertainty in this estimate) and with a dipolar contribution of 1000 cm^{-1}, Phillips could estimate *Dq* to be 1200 ± 400 cm^{-1} in agreement both with experiment and with Van Vleck's original result.

Our results, as discussed in the preceding section, show that these conclusions must be seriously modified. As we have seen, the dipolar contribution cannot by itself yield a value for the crystalline field strength in agreement with observation even though based on a model which augments the dipole moment by a large factor. This result contradicts Phillips' conclusion since if all the terms arising from the finite extension of the ligand charge density do cancel each other then we are left with a dipolar contribution (370 cm^{-1}) and hence a *Dq* which is still far from the measured value[21] (1750 cm^{-1}). Suppose instead that one accepts the assertion that the crystalline field is adequately described by a potential such as V_{eff} of Eq. (9). If we consider the contributions to *Dq* coming from V_p ($+370$ cm^{-1} and V_L (-320 cm^{-1}) as having been determined correctly by our calculations, then an orthogonalization contribution (V_R) of 1700 cm^{-1} is needed in order to obtain a theoretical *Dq* in agreement with experiment. This value is remarkably close to the value assumed by

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[23] J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959).

[24] F. Quelle (unpublished).

Phillips, but since his value was determined (actually chosen) so as to cancel out Kleiner's calculated overlap contribution (-1500 cm^{-1}) we must call the agreement accidental.

Thus, Phillips' procedure, while highly attractive, does not appear completely adequate. Let us examine it in more detail. Phillips' conclusions were based on observations made during an orthogonalized plane wave calculation for silicon.[23] In this method ψ_f is a plane wave and ϕ_{jlmn} are core functions and to a very good approximation are strictly orthogonal. For a transition metal salt it is not immediately apparent that the assumption of orthogonality between ϕ's belonging to different ions is valid. In fact Naiman[25] has obtained overlap integrals, appropriate to MnO, using free-ion Hartree-Fock functions for O^{-2} [26] and Mn^{+2}.[15] For an axis along an Mn-O line he obtained an $Mn(3d\sigma)-O(2p\sigma)$ overlap of 0.075 and for an O-O line an $O(2p\sigma)-O'(2p\sigma)$ (different centers) overlap of 0.110 and an $O(2p\pi)-O'(2p\pi)$ overlap of 0.044. He also observed that overlap integrals involving Mn^{++} $3s$ functions and O^{--} $2s$ functions tended to be appreciable. These results suggest that orthogonality between O^{-2} ions is as serious a problem as that between near neighbor Mn^{+2} and O^{-2} pairs. An orthogonal set of ϕ's could be constructed from the O^{-2} functions but using them would be very difficult. The terms which make important contributions in Eq. (10) are those whose E_{nl}'s are rather close in value to E (and thus must be accurately evaluated) *and* are those whose E_{nl}'s are most appreciably perturbed by interaction with neighboring ions and by the resolution of the orthogonality problem. Naiman's results suggest that the O^{-2} ion $2s$ and $2p$ E_{nl}'s may be as difficult to obtain as E. This in turn suggests that it would perhaps be wise to abandon the one-center single-ion-in-an-external-environment approach of the conventional crystalline field approximation and go to a molecular, multicenter approach. These considerations will be further discussed in the next section.

4. DISCUSSION

According to the crystalline field approximation, the effects arising from the rest of the crystal on the cation of interest may be taken into account by an electrostatic field. Yet, as we have seen, theoretical attempts at determining, within the framework of crystal field theory, accurate *a priori* values of the crystalline field strength have not been successful. The point charge or point dipole model seemingly gave good agreement with experiment but, as it turned out, mostly because improper $3d$ wave functions were used. Attempts at acknowledging the distribution in space of the electrons, as in Kleiner's calculation, resulted in a very poor result (despite the improvement that was obtained in the present work). The further refinement of including orthogonalization in the calculation led Phillips to a very attractive procedure, which upon closer examination has been shown to be inadequate. Each successive refinement seems to lead to more difficulties.

Although the over-all agreement with the predictions of crystal field theory is fairly good, there has been increasing experimental evidence which reveals discrepancies.[27] Such quantities as spin-orbit coupling, hyperfine interaction, and g values are found to differ from their free-ion values,[28] and this has been interpreted to indicate that electron transfer must play an appreciable role.[5,7] Covalent bonding effects have been introduced by Stevens[29] and Owen[30] and experimentally confirmed by the results of Tinkham[31] and Griffith *et al.*[32] For all these reasons it is clear that some of the basic assumptions of a static crystalline field must be questioned; the $3d$ wave functions do overlap—each other and the ligand wave functions—and so the surrounding ions cannot be treated as simply point charges. Since the overlap is in fact fairly large,[25] one may not treat the $3d$ wave functions as purely atomic orbitals based on a naive ionic model. A more appropriate picture is to consider the $3d$ functions as belonging to the entire complex—a computationally difficult task.

Paralleling the long history of crystal field theory have been several other theories, of which Pauling's[33] valence treatment and the molecular orbital approach of Van Vleck[34] have been the most prominent. (The calculation of Tanabe and Sugano[12] appears to have been the only attempt to use molecular orbital theory in a quantitative calculation for Dq.) Each has had its share of successes and failures. They serve to point out that comparisons of the different methods suggest certain necessary modifications in crystal field theory itself. Perhaps the most successful approach to date has resulted from the union of crystal field theory and molecular orbital theory; it is called ligand field theory. This union is considered artificial. Jarrett[35] has recently suggested a generalization of crystal field theory which includes covalent bonding in such a way as to allow for a range from purely ionic to strongly covalent bonding, thereby providing a bridge between the various theories. Unfortunately, Jarrett's formalism, while mathematically powerful, appears to make a practical application

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[25] C. Naiman, Quarterly Progress Report, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, July 15, 1960 (unpublished).

[26] R. E. Watson, Phys. Rev. **111**, 1108 (1958).

[27] Among the first to point out such discrepancies were A, Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A206**. 164 and 173 (1951), and J. H. Griffiths and J. Owen, Proc. Roy. Soc. (London) **A213**, 459 (1952). See also reference 7.

[28] J. Owen, Proc. Roy. Soc. (London) **A227**, 183 (1955).

[29] K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 542 (1953).

[30] J. Owen, reference 28, and Discussions Faraday Soc. **19**, 127 (1955).

[31] M. Tinkham, Proc. Roy. Soc. (London) **A236**, 535 (1956).

[32] J. H. E. Griffiths, J. Owen, and I. M. Ward, Proc. Roy. Soc. (London) **A219**, 526 (1953).

[33] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), 2nd ed.

[34] J. H. Van Vleck, J. Chem. Phys. **3**, 807 (1935), and elaborated upon by J. Owen, reference 28.

[35] H. S. Jarrett, J. Chem. Phys. **31**, 1579 (1959).

computationally formidable and perhaps not at all tractable.

Aside from the above well-known modifications of crystal field theory, which appear necessary if agreement is to be achieved, there are a number of other difficulties which enter even on the simple ionic picture of the crystalline field approximation. Of these, we shall briefly mention a few since these are not usually discussed. The use of the strong-field representation leads to the use of orbitals designated by cubic quantum numbers (t_{2g} or e_g for d electrons in cubic fields) rather than the spherical quantum numbers, m_l. These strong-field functions are the correct functions to use only if the Hamiltonian is solved *without* the spin-orbit and the electron interaction terms (e^2/r_{ij}). Except in rare circumstances this limit is not approached. Nevertheless, use is made of the strong-field orbital description with the further restriction that the radial wave functions for the t_{2g} and e_g electrons be identical not only with the free-atom values but with *each other* as well. Recent calculations and neutron diffraction experiments[36–39] have suggested that these assumptions are not correct. There are a number of effects, which arise out of a potential of the type given in Fig. 2, which perturb the radial wave functions—first from their usual free-ion values[17,40] and secondly, so as to cause a splitting in the t_{2g} and e_g functions such that their radial functions are not identical.[41] In addition if one does calculations for an ion in two different states, the one-electron wave functions vary appreciably.[15,17] Yet, basic to the interpretation of optical absorption spectra is the assumption that a single radial wave function suffices for all the t_{2g} and e_g electrons in both their ground and excited states. As has been discussed by Koster,[42] there is the assumption of separability of the one-electron wave functions into products of radial and angular factors when in fact separation is valid only for a spherical environment. Thus, unlike the usual assumption underlying the theory, there need not be any special relationship between the t_{2g} and e_g electrons (such as common radial function or separability into radial and angular parts.)

Finally, the preceding discussion was based on a many-electron wave function which is either a single configuration (Hartree-Fock) wave function or a linear combination of a small number of configurations. In the case of the free iron series ion multiplet spectra, there are systematic discrepancies between Hartree-Fock predictions and experiment. It appears that an approach to the 'correlation' problem, such as configuration interaction, is necessary for an appreciable improvement of theoretical predictions. One might suspect that a similar (*many* configuration) configuration interaction treatment is necessary for the case of an ion in a crystalline field as well.[43]

5. CONCLUSION

We have concerned ourselves with discussing various attempts at determining from first principles accurate theoretical values of the crystalline field strength. We have seen that none of these have been successful and that each successive refinement has introduced new difficulties. It is not certain that a more "correct" (but not complete) treatment would yield better results. Certainly, the crude point charge model is incorrect and attempts to justify this method appear destined to fail. Both experimental and theoretical evidence for the inadequacy of the electrostatic potential theory were reviewed and discussed and some of the required modifications indicated. These lead us to conclude that while crystal field theory, when used as a semiempirical theory, has on the whole had a high degree of success, it appears impossible to justify on theoretical grounds some of its basic premises. It therefore cannot be considered to be a *fundamental* theory for the description of the wide range of phenomena that as a semiempirical method it has dealt with so well. What is needed is a theory based on an essentially molecular, many-center, many-configuration approach. In such a treatment symmetry will of course play as essential a role as it does in the simpler theories, but the necessary computations (including many-center integrals) will be much more complex than the integral of Eq. (1).

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[36] R. E. Watson, Phys. Rev. **117**, 742 (1960).

[37] A. J. Freeman and R. E. Watson, Phys. Rev. **118**, 1168 (1960) and J. Appl. Phys. **31**, 374S (1960).

[38] J. M. Hastings, N. E. Elliott, and L. M. Corliss, Phys. Rev. **115**, 13 (1959).

[39] R. Nathans, S. Pickart, and H. Alperin, Conference on Neutron Diffraction in Relation to Magnetism and Chemical Bonding, Gatlinburg, Tennessee, April 20, 1960 (unpublished).

[40] See reference 37, appendix, for a discussion of the tendency of the electrostatic crystalline field to expand the $3d$ functions. If we estimate the magnitude of this expansion effect according to the method of reference 37, we would find a $3d$ wave function which falls roughly half way between the Cr^{+3} functions of Watson[15] and the Cr^{+2} function[19] illustrated in Fig. 3. While this pseudo-$3d$ function would change the numerical values of the calculated contributions to Dq (see Sec. 2), the conclusions arrived at in this paper would not be materially changed.

[41] The calculations of references 36 and 37 led to a prediction that even a half-closed-shell ion like Mn^{++} would have a nonspherically charge density and hence a form factor which, when calculated according to the methods of R. J. Weiss and A. J. Freeman [J. Phys. Chem. Solids **10**, 147 (1959)], would show measurable asymmetries. Such asymmetries have been suggested for Mn^{+2} [37] and observed for Fe^{+3} in Fe_3O_4.[39]

[42] G. F. Koster, Quarterly Progress Report, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, January 15, 1960 (unpublished), and to be published.

[43] Some of these ideas have also been discussed in the writings of C. K. Jorgensen [in particular, see Discussions Faraday Soc. **26**, 110 (1958)].