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Effect of Crystalline Fields on Charge Densities and Magnetic Form Factors*

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The effects of crystalline fields on $3d$ charge densities and magnetic form factors for transition metal ions are discussed on the basis of recent theoretical investigations augmented by an analysis of optical absorption data. It is shown that the crystalline field has two effects on the free ion $3d$ wave functions and hence on their form factors as well: (1) a differentiation or "splitting" of the two types of cubic $3d$ functions by an expansion of the $t_{2g}(e_g)$ orbitals and a contraction of the $e_g(t_{2g})$ orbitals resulting in two different radial charge densities, and (2) a net expansion of the charge distribution from the free ion value. The magnetic form factors due to this "splitting" effect when calculated according to the methods of Weiss and Freeman show measurable deviations from the free atom results. A form factor for Mn^{+2} based on optical absorption data shows a large expansion of the $3d$ charge density, in agreement with the magnetic form factor measurements of Hastings, Elliott, and Corliss. This agreement, based on the use of theoretical $F^k(3d,3d)$ integrals, indicates that the well-known discrepancy between theoretical and experimental values of these integrals arises from the fact that the quantities obtained experimentally are not true $F^k(3d,3d)$ integrals. The crystalline potential due to an array of negative ion charge densities has been employed to discuss these various effects and their meaning with respect to a proper (essentially molecular) treatment.

INTRODUCTION

WEISS and Freeman[1] have calculated the effect on form factors of nonspherical charge distributions in various crystalline environments. They showed that large measurable deviations from the usual spherical approximation resulted, and that a theoretical analysis of these "bumps" in measured form factor data led to a new technique for determining the spatial symmetry of the spin densities in magnetic materials. By applying this technique to the precise polarized neutron measurements of Shull, Nathans, and collaborators,[2] they were able to determine the angular distribution of the $3d$ spin densities in Fe, Ni, and (fcc) Co in terms of a mixing of the two types of $3d$ wave functions in a cubic field (i.e., a triply degenerate set, called t_{2g} and a doubly degenerate set, called e_g). Recently Pickart and Nathans[3] have carried out a similar analysis of their detailed measurements of the Fe_3Al form factor. In these papers[1,3] the usual assumption of a single radial wave function for both the t_{2g} and e_g electrons about a given atom site was made. (For Fe_3Al, which has two types of Fe atom sites at which the Fe atoms have different magnetic moments and hence different spin densities, a distinct radial wave function for each site was of course needed to analyze the measured magnetic form factor.[3])

In this work theoretical form factors calculated from free atom (or ion) wave functions are used. The purpose of this paper is to investigate the effects of crystalline fields on the free atom wave functions and in turn on the theoretical form factors. Our discussion is specialized to the case of a transition metal ion in an ionic compound where the effects of a crystalline field are expected to be large. The results of this study suggest that reciprocally, measurements of the magnetic form factor would provide us with information about the crystalline field as well.

WAVE FUNCTIONS FOR AN ION IN A CRYSTALLINE FIELD

If, in an ionic crystal of cubic symmetry, we computed the potential at the site of a metal ion due to the rest of the ions in the crystal and then used this (external) potential in a calculation of the metal ion's wave functions, two effects would be observed (see Appendix I). First, there would be a differentiation or "splitting" of the two types of cubic $3d$ functions [by an expansion of the t_{2g} (or e_g) orbital and a contraction of the e_g (or t_{2g}) orbital] with respect to their common free ion value, resulting in two different *radial* charge densities. Second, this splitting would be accompanied by a net expansion of the ion's charge distribution as compared with the free ion's charge distribution—the expansion being most noticeable in

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[1] R. J. Weiss and A. J. Freeman, J. Phys. Chem. Solids, **10**, 147 (1959).

[2] R. Nathans, C. G. Shull, G. Shirane, and A. Andresen, J. Phys. Chem. Solids **10**, 133 (1959); R. Nathans and A. Paoletti, Phys. Rev. Letters **2**, 252 (1959).

[3] S. Pickart and R. Nathans, presented at the *Fifth Conference on Magnetism and Magnetic Materials, Detroit, November, 1959* [J. Appl. Phys. (to be published)].

the outermost electron shell (namely the 3*d* shell in our case).[3a]

One of us[4] has recently carried out a Hartree-Fock calculation for the $\text{Mn}^{+2}(3d^5)$ ion in an external cubic point charge field. This calculation gives some quantitative indication of the importance of the first crystalline field effect (i.e., the 3*d* splitting) but due to the crude crystalline field used gives no information about the magnitude of the second effect (i.e., expansion of the radial charge density). In what follows, we use the results of this calculation, augmented by experimental optical absorption data, to estimate and discuss the variation in form factors due to both these effects.

EFFECT OF 3*d* SHELL SPLITTING ON THE MAGNETIC FORM FACTOR

For *d* electrons in a cubic crystalline fields, Weiss and Freeman[1] showed that the form factors of the two types of cubic *d* functions, t_{2g} and e_g, could be expressed in the form

$$f(t_{2g}) = \langle j_0 \rangle - A(hkl)\langle j_4 \rangle,$$
$$f(e_g) = \langle j_0 \rangle + \tfrac{3}{2}A(hkl)\langle j_4 \rangle, \qquad (1)$$

where $\langle j_n \rangle$ denotes the integral of the product of the radial charge density and the *n*th spherical Bessel function, and the coefficients $A(hkl)$ contain the orientation dependence of the form factors at the Bragg reflections (hkl) for which scattering occurs. Since $\langle j_0 \rangle$ is the usual spherically symmetric form factor, the second term in Eq. (1) gives rise to deviations from a smooth curve which would be observed as "bumps" in magnetic form factor measurements. These authors further showed that an analysis of these "bumps" led to a determination of the spatial symmetry of the outer electrons in magnetic materials.

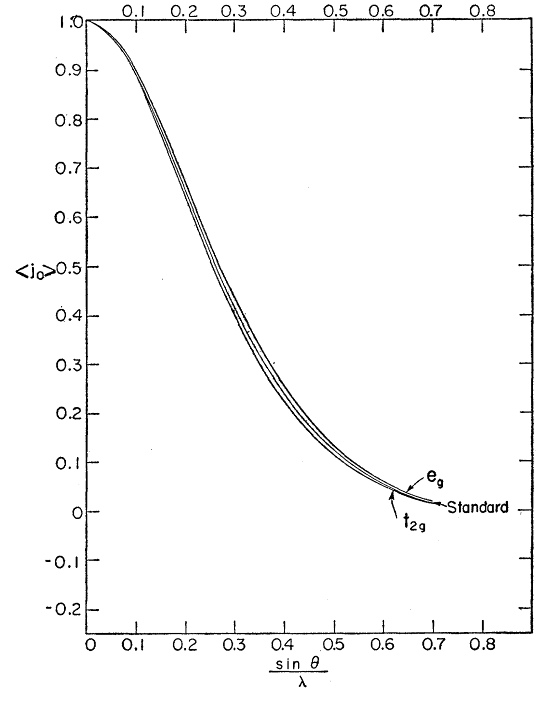

FIG. 1. The "splitting" effect on the calculated $\langle j_0 \rangle$ part of the form factor for the t_{2g} and e_g electrons along with the free atom result (labeled "standard").

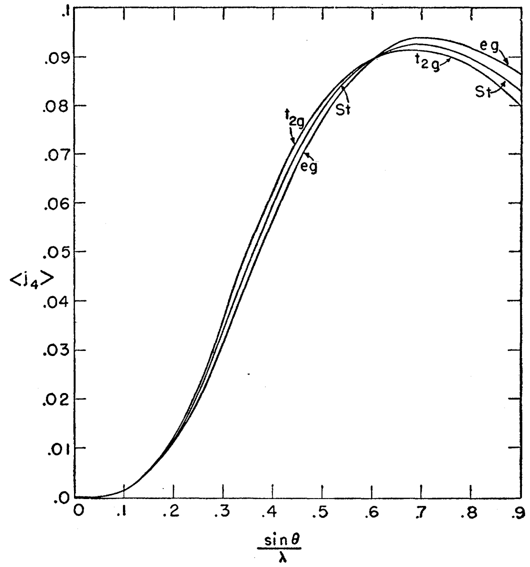

FIG. 2. The "splitting" effect on the calculated $\langle j_4 \rangle$ part of the form factor for the t_{2g} and e_g electrons along with the free atom result (labeled "St.")

In the Hartree-Fock calculation mentioned above, the external potential was due to an octahedral array of negative point charges. The individual electrons were taken to have cubic symmetry (the "strong field" approximation) and different radial wave functions were obtained for the two types of cubic 3*d* electrons. We have calculated the effect of this "splitting" on the magnetic form factor using the two cubic 3*d* radial charge distributions obtained by Watson.[4] The calculations were carried out on Whirlwind I, using procedures and routines described earlier.[5] In what follows, we use the results of a free ion Hartree-Fock calculation[6] for Mn^{+2} as a reference frame for our considerations.

The "splitting" of the free atom 3*d* charge density by the crystalline field is reflected in the splitting of the $\langle j_0 \rangle$ and $\langle j_4 \rangle$ parts of the form factor [see Eq. (1)], as is shown in Figs. 1 and 2, respectively, as a function of $\sin\theta/\lambda$ in A^{-1} units.

As observed in earlier work,[1] the form factors for the

[3a] W. Marshall [Bull. Am. Phys. Soc. 4, 142 (1959)] has pointed out that an expansion of the 3*d* charge density would produce agreement with several pieces of experimental data (including neutron diffraction).

[4] R. E. Watson, Quarterly Progress Reports, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, July 15, 1959 (unpublished), p. 3; and Phys. Rev. **117**, 742 (1960).

[5] See A. J. Freeman, Acta Cryst. 12, 261 (1959), for complete details.

[6] R. E. Watson, Phys. Rev. **118**, 1036 (1960); and Technical Report No. 12, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, June 15, 1959 (unpublished).

individual t_{2g} and e_g electrons calculated at the Bragg reflections in a cubic crystal fail to lie on a smooth curve. The use of different radial wave functions in Eq. (1) gives rise to *further* deviations or "bumps" from a smooth form factor curve at the observed Bragg peaks—deviations which are due to the radial charge differences alone. These "new" deviations cannot be described by a simple scaling of the free atom deviations since for some reflections the "bumps" are increased while for others they are diminished. These deviations from the free atom values have a magnitude of the order of 0.02 electron units [which is well above the experimental uncertainty (0.002) in current polarized neutron measurements],[2] or of the order of some "bumps" due to free atom nonsphericity alone. From this we see that in these cases a single form factor for both the e_g and t_{2g} electrons cannot give a unique determination of the spatial symmetry of the outer electrons, and an analysis along the lines suggested in this paper becomes necessary.

Koster has pointed out to us that this *3d* "splitting" mechanism may explain an observed absorption line in a manganous perchlorate solution.[7] The Mn^{+2} ion with its half-filled shell is a special case which would allow this effect to be seen since for nonclosed (but not half-filled) *3d* shell ions there are many other effects which interfere with this observation.

As a free ion the Mn^{+2} ground state is $(3d)^5$, ^6S which has a spherical charge distribution and hence its form factor would be the usual (spherically symmetric) smooth curve. The "splitting" effect however results in a nonspherical charge distribution which gives a form factor which shows deviations from a smooth curve even though three t_{2g} orbitals and two e_g orbitals are occupied (i.e., a half-filled shell). The "bumps" in the total form factor for these five cubic *3d* electrons, which is the least favorable case that could be considered, are not as large as the ones discussed earlier for the separate t_{2g} or e_g form factors—they are just outside of experimental uncertainty—and hence would be hard to observe. For transition metal ions with nonclosed (but *not* half-filled) *3d* shells this effect would be more readily observed.

Deviations from a smooth form factor curve have been observed by Hastings, Elliott, and Corliss[8] for Mn^{+2} in several ionic compounds. From their results we have investigated their measured form factors for αMnS and MnO [since they both have the same (NaCl) structure]; these are shown in Fig. 3. The observed deviations are larger than the values calculated by us for these Bragg reflections on the basis of the "splitting" of the cubic *3d* wave functions for a charge density made up of five *3d* electrons. It therefore appears that there are additional mechanisms which are contributing to these deviations (e.g., covalency effects). However, in agreement with our analysis, the observed deviations in the form factors show the same qualitative behavior [i.e., at common reflections in Fig. 3, both MnO and αMnS have the same relationship with respect to the smooth (spherically symmetric) curve].

EFFECT OF WAVE-FUNCTION EXPANSION ON THE MAGNETIC FORM FACTOR

Since a point charge cubic field does not produce a charge density expansion in a half-filled *3d* shell ion (a more appropriate handling of the crystalline problem would do this[9]), the results of the calculation based on the octahedral array of point charges described earlier cannot be used to discuss the effect of charge density expansion on the form factor. For this reason we have looked into the information available from optical absorption data for transition metal ions in crystalline environments. This data[10] indicates that there are radical changes in the crystalline *3d* charge distribution from the free ion values.

In both the free ion and crystalline ion absorption work two parameters are interpreted to be integrals involving the *3d* wave functions *alone*. These are the Slater $F^k(3d,3d)$ integrals.[11] These integrals are found to be substantially smaller for the crystalline ions and this can be interpreted as representing a substantial expansion of the atomic *3d* radial function. We have taken a typical observed variation (about 15%) in the

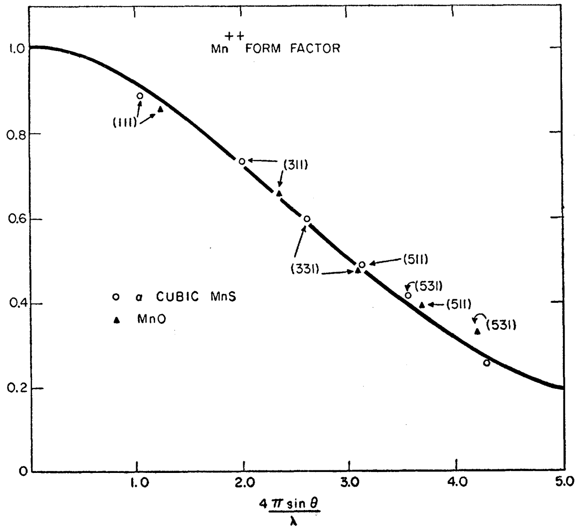

FIG 3. The magnetic form factor for Mn^{++} in MnO (▲) and α cubic MnS (○) as determined by Hastings, Elliott, and Corliss. The smooth curve was obtained by these authors by scaling the free atom Hartree-Fock result by a factor of 0.9.

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[7] L. J. Heidt, G. F. Koster, and A. M. Johnson, J. Am. Chem. Soc. **80**, 6471 (1958).

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

[9] See Appendix I for a discussion of this.

[10] For example see C. K. Jorgensen, Discussions Faraday Soc. **26**, 110 (1958).

[11] See E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1953), in particular Chap. IV.

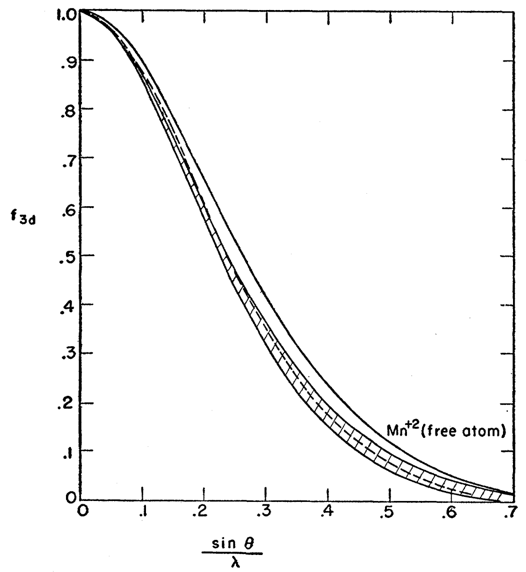

FIG. 4. The calculated Mn^{++} free atom form factor, the predicted crystalline Mn^{++} form factor from optical absorption data (shaded region), and the measured magnetic form factor of Hastings et al. (dashed curve).

$F^k(3d,3d)$ integrals for Mn^{+2} and from tabulated theoretical $F^k(3d,3d)$ integrals for the iron series ions[6] we have selected $3d$ wave functions which show this same percentage change in $F^k(3d,3d)$ from the theoretical Mn^{+2} free ion value. The V^{+2} and Mn^+ $3d$ functions satisfy this requirement. Their form factors, along with that for the free Mn^{+2} ion,[12] are plotted in Fig. 4. The region between the V^{+2} and Mn^+ form factors has been shaded to indicate a range in predicted form factor due to the expansion effect of the crystalline field. If we now also plot the observed Mn^{+2} magnetic form factor, as determined by Hastings, Elliott, and Corliss[8] for a variety of Mn compounds, we see that there is good agreement with our crude estimate made from the optical absorption data. This agreement suggests that both the optical absorption data and the neutron diffraction data can be understood as being due to an expansion of the $3d$ wave function from its free ion value.

It is to be noted that the $3d$ functions used in this form factor estimate have $F^k(3d,3d)$ values which are *not* in agreement with experimental optical absorption data $F^k(3d,3d)$'s. This is due to the fact[6] that theoretical and experimental $F^k(3d,3d)$'s for the same ion just do not match. The fact that our estimate of the form factor agrees well with the Hastings, Elliott, and Corliss experimental one suggests that the $F^k(3d,3d)$ discrepancy is *not* due to a difference between the theoretical and the actual $3d$ radial dependence but is instead due to the fact that the quantities measured by experiment are not true $F^k(3d,3d)$ integrals and in turn that we must go beyond a Hartree-Fock description of the atom if we are to have a detailed understanding of the measured quantities.

ACKNOWLEDGMENTS

We are indebted to Professor C. G. Shull, Professor G. F. Koster, and Dr. R. J. Harrison for helpful discussions and to Dr. J. M. Hastings for making his data available to us.

APPENDIX I. Mn ION IN CRYSTALLINE FIELDS

The Hartree-Fock calculation[4] for Mn^{+2} in an octahedral array of point charges gave no estimate of the tendancy of crystalline environments to expand $3d$ functions. It seems worthwhile to discuss this briefly and to discuss what might be done to improve on this calculation.

It was noted[4,13] that the presence of an octahedral array of ions about an Mn^{+2} ion produces a spherical potential, V_0, which interacts with all the Mn^{+2} electrons and a cubic potential, V_4, which interacts with only the $3d$ electrons. The spherical potential (V_0) due

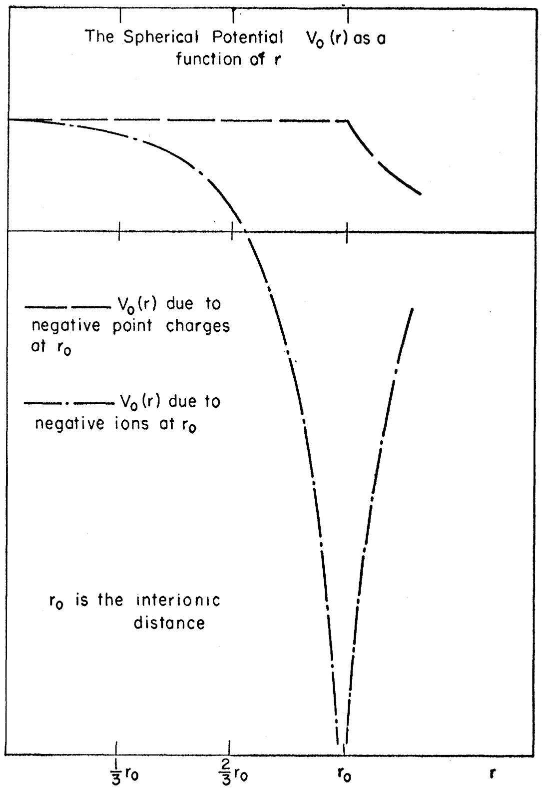

FIG. 5. The spherical potential $V_0(r)$ as a function of r due to: (a) negative point charges at r_0, the interionic distance (full dashed curve) and (b) negative ions at r_0 (broken dashed curve).

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[12] R. E. Watson and A. J. Freeman, Acta Cryst. (to be published).

[13] Similar investigations along this line have been made, e.g., R. Linn Belford and N. Karplus, J. Chem. Phys. 31, 394 (1959), who treated the problem of a square array of four point charges about an iron series ion.

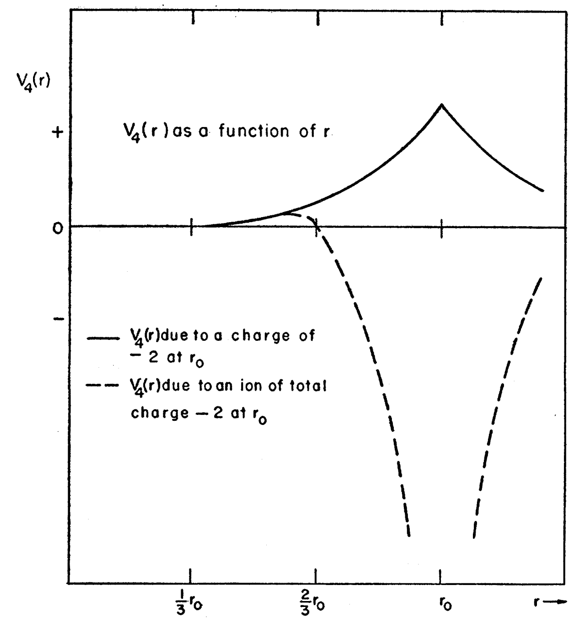

FIG. 6. The $V_4(r)$ part of the potential due to: (a) a point charge of -2 at r_0 (solid curve) and (b) an ion of total charge -2 at r_0 (dashed curve).

to (a) an octahedral array of point charges and (b) the charge density of an octahedral array of negative ions is illustrated in Fig. 5. The figure illustrates why the point charge potential did not encourage the 3d function to expand whereas the ion potential does. The cubic potential (V_4) is illustrated in Fig. 6 for both the point charge and the ion environments; these are drawn for a direction pointing toward the neighboring ions (as do the doubly degenerate, e_g, electrons). The cubic potential has the opposite sign for the directions in which the triply degenerate, t_{2g}, functions point. This is the cause of the *3d* shell "splitting" effect mentioned in the text. The sign of experimental crystalline field splittings tells us that it is the inner loop (of positive sign in the figure) which predominates.

Proper handling of a calculation for an Mn^{++} ion surrounded by six negative ions requires that the Mn^{++} and the negative ion one-electron functions be orthogonal to one another. Failure to do this would encourage part of the Mn^{++} electronic charge to occupy the wells at the sites of the negative ion nuclei which are already occupied by the negative ions' core electrons.

One of us (R.E.W.) has investigated the potential for an Mn^{++} ion surrounded by an octahedral array of six O^{-2} ions[14] at a distance appropriate to the MnO crystal. An appreciable part of the $Mn^{++}3d$ charge density penetrates into the deep wells and a Hartree-Fock calculation for Mn^{++} in such an environment (without orthogonalization) would yield meaningless results. In other words, orthogonalization cannot be neglected. Its inclusion turns the calculation into essentially a molecular problem. Unfortunately, the molecular calculation is considerably more difficult than a calculation for an ion in an external field. To date no such molecular Hartree-Fock calculation has been reported (either for the simple case of an iron series ion and its nearest neighbors or a proper crystal calculation).

The results for the Mn^{+2} ion when solved for in the O^{-2} ion field are not without interest for they and the point charge field results serve as bounds on the behavior of the results of calculations of this sort. The O^{-2} ion field yields a *3d* charge density which is shifted outwards from the free ion value and in turn this results in a contraction of the *3d* form factor. This contraction of the *3d* form factor relative to the free ion value is between three and four times that observed experimentally.[8]

Some readers may believe that the solution to the orthogonality problem is to modify the ion potential so that the deep wells disappear (or at least decrease in magnitude) while keeping that part of the potential near the Mn nucleus essentially unchanged. A calculation for such a potential would yield a result between those of the point charge and the unmodified ion charge fields. Thus an appropriately *chosen* potential would yield an Mn^{++} ion whose *3d* form factor is in agreement with experiment and whose $F^k(3d,3d)$ integrals show the percentage changes which optical absorption data tells us are appropriate. This approach is at best dubious unless the modification is derived directly from the requirement of orthogonalization between one-electron functions on different ions.[15]

In conclusion, calculations for single ions in external fields can yield results which agree with experiments involving these ions in crystals but the ability of theory to predict the experimental results will not be truly tested until (as indicated above) a proper, essentially molecular, calculation is done.

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

[15] *Note added in proof.*—J. C. Phillips [J. Phys. Chem. Solids **11**, 226 (1959)] has recently discussed the role of orthogonality in crystal field calculations along the lines suggested by C. Herring [Photoconductivity conference, Atlantic City (1956) (John Wiley & Sons, Inc., New York, 1956), p. 86].