

Theory of the pressure dependence of a prototype exchange integral

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The variation of electron exchange integrals in solids subjected to hydrostatic pressures P is considered by examining a prototype exchange integral J . The quantity $(1/J)(dJ/dP)$ is determined within the context of a theory of solids under hydrostatic pressures in which the application of pressure is represented in terms of the crystal compressibility and two parameters which are associated with electronic screening and wave-function-distortion effects. Pressure variations of magnetic-phase boundaries, exchange-enhanced susceptibilities, and exchange interactions of pairs of Cr^{3+} ions in ruby are considered as examples of the applications of the results.

I. INTRODUCTION

The development of the diamond anvil cell^{1,2} and the ruby pressure scale³⁻⁴ has made the attainment of measurements at large hydrostatic pressures (~ 100 kbar) a routine operation. As a consequence, the investigation of the variation of properties of solids as a function of pressure has become an increasingly employed experimental research technique. To obtain the full utility of the method, one should understand what effects are produced microscopically in the solid due to the applied pressure.

It is clear that the volume of the unit cell, or the internuclear distance, should change with increasing pressure, but is this a sufficient representation of pressure? It appears^{2,4,5-9} that other features must be significant, the most important of which ought to be electron-screening effects and wave-function distortions. Such features can be expected to be significant in the production of frequency shifts in optical spectra and in the production of bandwidth and gap variations in band structures.

One example which clearly emphasizes the inadequacy of a compressibility-only pressure theory is given by the behavior of the ruby R lines. The interparticle distances can be varied by applying pressure at constant temperature or by increasing the temperature at constant applied pressure. The former approach decreases the interparticle distances, while the latter increases them. In both cases, the frequency shifts of the R lines are in the same direction.^{4,10,11} Thermal-frequency shifts are well understood¹⁰ theoretically, while the pressure shift is in the wrong direction if only compressibility is considered in a point-charge model in crystal-field theory.

To obtain a physical picture of other effects that can occur when pressure is applied, imagine a single ion surrounded by a crystal lattice. The

application of pressure causes the lattice to press in on the ion, and as a result, the electron cloud of the ion can be expected to shrink or distort in response. This suggests that there can be two charge related effects: (i) The wave function of the ion of interest is subject to distortion; and (ii) the electron cloud distribution giving rise to a crystal field can also be disturbed, so the crystal field strength can be correspondingly perturbed.

In a previous work,¹² a theoretical treatment of the frequency shifts of five transitions of the single Cr^{3+} ion spectra of ruby has been presented with satisfactory results. In this theory, two parameters, $\Lambda(P)$ and $\Omega(P)$, are introduced in addition to the crystal compressibility to represent the effects of pressure as an effective change in interaction strengths (scaling hypothesis). To see how this comes about, consider the following. Before a pressure is applied, the system is characterized by a Hamiltonian H_0 , a state space on which H_0 acts, and subsidiary conditions such as boundary conditions and the requirement of thermal equilibrium. After pressure is applied, a new Hamiltonian $H(P) = H'_0 + V(P)$ can be used where H'_0 is the same as H_0 except that equilibrium parameters in H_0 are replaced by their new values at pressure P . The pressure potential $V(P)$ contains any explicit pressure dependence, and $V(0) = 0$.

If the pressure potential is set equal to zero for all P , the resulting approximation is the one in which only a volume effect, or a change of interparticle distances, occurs. Hence, $V(P) \neq 0$ must account for the charge related pressure effects. Suppose now that the system described by $H(P)$ is allowed to be formed as a condensation of loose atoms. In this "equivalent pressure free" system, it is clear that the interparticle interaction strengths must be modified from those of the initial system. These two thoughts are combined if one postulates a scaling of the charge related

coupling constants which can be written in the forms $e^2 \rightarrow \Lambda(P)e^2$ and $Z \rightarrow \Omega(P)Z/\Lambda(P)$. The quantity e^2 is the square of an electronic charge and Z is the effective charge number of the nuclear unit (which may include closed electron shells). This mapping is equivalent to saying that $V(P)$ is a sum of pairwise Coulombic potentials $V_{ij}(P) = -\lambda_i(P)\lambda_j(P)/r_{ij}$, with $(\lambda_e/e)^2 = 1 - \Lambda(P)$ and $(\lambda_e/e)(\lambda_n/Z_n e) = \Omega(P) - 1$. The result is an energy-level scheme at pressure $P > 0$ that is simply isomorphic to the $P = 0$ scheme.

Although $\Lambda(P)$ and $\Omega(P)$ are introduced as formal mapping parameters, their physical interpretations are the desired screening and distortion features noted above. $\Lambda(P)$ is associated with electronic screening since the ion-crystal field interaction is scaled by the mapping $e^2 \rightarrow \Lambda \times (P)e^2$. $\Omega(P)$ is associated with wave-function spread or distortion. For example, following Ref. 12, one finds, for ruby, $(1/\langle r \rangle)d\langle r \rangle/dP \approx -d\Omega/dP$, so that variation¹³ of the radial extent of the electron cloud is determined by $\Omega(P)$. Thus, $\Lambda(P)$, $\Omega(P)$, and the crystal compressibility, $\kappa = -(1/V)dV/dP$, provide a representation of the more important features of the application of pressure.

In this paper, an attempt is made to use this scaling theory to estimate the effect of hydrostatic pressure on electron exchange integrals and to determine, in particular, the extent to which exchange is affected by the screening and distortion parameters Λ and Ω .

An understanding of the variation of exchange integrals is relevant to numerous physical properties since exchange is an inherent part of many-electron systems. For example, in the theory of magnetism, magnetic phase boundaries are often discussed in terms of bilinear electron (Heisenberg) exchange and sometimes biquadratic electron exchange. It has been assumed that the details of these boundaries in the exchange parameter space for any particular magnetic sample are rather academic since the exchange integrals are constants. However, under the application of large hydrostatic pressures, small variations of exchange integrals can be produced. Consequently, it is possible that small regions of the exchange parameter space can be explored if the variation of the exchange integrals can be distinguished from other pressure effects.

Closely related to the study of magnetic phase boundaries is the occurrence of exchange-enhanced Van Vleck susceptibilities that have been noted⁶ in some singlet-ground-state rare-earth compounds. In these systems, the Van Vleck susceptibility provides information on the crystal-field splitting of the ground state and the first ex-

cited state. If the susceptibility is exchange enhanced, the variation of the exchange parameter with pressure must be known before the variation of this splitting can be fully analyzed.

Interatomic exchange interactions also occur directly in the study of optical spectra. Especially interesting is the study of the spectra of impurity ions in a solid host. At low concentrations of the impurity, the spectra of a single ion in the crystal field of the host is observed. Increasing the concentration eventually leads to interacting pairs of impurity ions in which case an exchange interaction can be involved.

Each of the foregoing situations is considered in Sec. III on the basis of the results for the pressure variation of exchange determined within the context of the scaling theory of solids under hydrostatic pressures. The latter analysis is given in Sec. II. In Sec. III, the variation of a magnetic phase boundary is discussed as a change in the mean-field-theory Curie temperature. Second, exchange enhancement of susceptibilities is considered in the form¹⁴ $\chi_m = \chi/(1 - \lambda\chi)$. Third, a specific application to optical spectra is presented for interacting pairs of Cr^{3+} ions in ruby.

II. PRESSURE-DEPENDENT EXCHANGE

Consider an exchange integral defined at zero pressure to be

$$J = \int d^3r_1 d^3r_2 \psi_i^*(\vec{r}_1) \phi_j^*(\vec{r}_2) \frac{e^2}{r_{12}} \psi_i(\vec{r}_2) \phi_j(\vec{r}_1). \quad (1)$$

The wave function $\psi_i(\vec{r}) = \psi(\vec{r} - \vec{r}_i)$ is a one-electron state at site i , and $r_{12} = |\vec{r}_1 - \vec{r}_2|$. We seek the pressure dependence of expression (1) in the form $(1/J)dJ/dP$ which is to be approximately determined as a function of Λ , Ω , and the compressibility κ . The ratio of J and its pressure derivative is used so that we do not become involved with the detailed difficulties of evaluating expression (1). One might expect the dependence of the ratio on the compressibility and the scaling parameters to be more accurately obtained from roughly approximated wave functions than could be J itself since $(1/J) \times dJ/dP = d(\ln J)/dP$, and the logarithm varies slowly. Use of the ratio also preserves for J its usual role as a phenomenological parameter at $P = 0$.

For the moment, let us assume that the one electron states ψ and ϕ have been determined by, e.g., a Hartree-Fock self-consistent-field theory. We make the reasonable assumption that the fractional variations of these functions can be written as functions of κ , Λ , and Ω , i.e.,

$$\frac{1}{\psi} \frac{\partial \psi}{\partial P} \approx f(\kappa, \Lambda, \Omega), \quad (2a)$$

$$\frac{1}{\phi} \frac{\partial \phi}{\partial P} \approx g(\kappa, \Lambda, \Omega). \quad (2b)$$

Next, note that the number r_{12} in definition (1) contains an implicit dependence on the distance between the interacting ions and, hence, the compressibility. This dependence could be shown explicitly if the integration variables were chosen such that $\vec{r}_1 = 0$ at site i and $\vec{r}_2 = 0$ at site j . Then, $r_{12} = |(\vec{r}_1 - \vec{r}_2) + (\vec{r}_i - \vec{r}_j)|$, and we have

$$(1/r_{12})^{-1} d(1/r_{12})/dP \approx \frac{1}{3} \kappa. \quad (3)$$

Allowing for screening, the pressure variation of J is produced by differentiating Eq. (1) with respect to P . Taking $\vec{r}_i = 0$,

$$\begin{aligned} \frac{1}{J} \frac{dJ}{dP} \approx & \frac{\kappa}{3} + 2f(\kappa, \Lambda, \Omega) + 2g(\kappa, \Lambda, \Omega) + \frac{d\Lambda}{dP} \\ & - \frac{\kappa}{3} \frac{1}{J} \int d^3r_1 d^3r_2 \psi^*(\vec{r}_1) \psi(\vec{r}_2) \frac{e^2}{r_{12}} \\ & \times [\vec{r}_j \cdot \nabla \phi^*(\vec{r}_2 - \vec{r}_j) + \vec{r}_j \cdot \nabla \phi(\vec{r}_1 - \vec{r}_j)]. \end{aligned} \quad (4)$$

Equation (4) gives the basic approximation of the pressure variation of the exchange parameter J . The functions f and g depend on the initial states ψ and ϕ and, consequently, depend on both the electronic configuration (quantum numbers $n\ell$) and the spacial configuration of the neighbors which give rise to the local crystal field. Numerical evaluations of f , g , and the last quantity in Eq. (4) could be obtained for specific cases if a perturbation approach were used with a model calculation; e.g., a point charge model could be used for the crystal field. Rather than follow this procedure here, we take a simpler approach which permits us to obtain an estimate of expression (4) in a useful analytical form.

Several approximations are used. Firstly, it is assumed that the major contribution to the wavefunction distortion occurs due to the radial part of the wave function, $R(r)$, so that $(1/\psi)(\partial\psi/\partial P) \approx (1/R)(\partial R/\partial P)$. This is appropriate for cases in which the site symmetry is unchanged or negligibly changed, as, e.g., in ruby.¹⁵⁻¹⁷

The second approximation is to select a radial wave function indicative of the exchanging electrons. For simplicity of presentation, a discussion appropriate for the ruby example is given here and generalized somewhat at the end. For Cr^{3+} , a $3d$ -type function is needed. We obtain an approximation by considering a hydrogenlike function.¹⁸ With the scaling parameters, the $3d$ radial function can be written

$$R(r) = \Omega^{7/2} e^{-(\rho/2)\Omega} R_{3d}(P=0), \quad (5)$$

$$R_{3d}(P=0) = [9(30)^{1/2}]^{-1} (Z/a_0)^{3/2} \rho^2 e^{-\rho/2}, \quad (6)$$

where $\rho = 2Zr/3a_0$, Z is the effective nuclear charge number, a_0 is the Bohr radius, and we have written $\Omega = 1 + \delta\Omega$.

Equation (5) holds specifically when the zero pressure function is given by Eq. (6). We rely on Eq. (6) to provide a guide to the selection of approximations, but the final results are stated in a form that does not depend on the explicit function (6). Assuming the Ω dependence in Eq. (5) is then somewhat better than a strictly hydrogenlike approximation.

From Eq. (5), we find

$$\frac{1}{R} \frac{\partial R}{\partial P} = \frac{1}{2} (7 - \rho\Omega) \Omega^{-1} \frac{d\Omega}{dP}. \quad (7a)$$

It would be quite natural to employ the approximation $\rho \approx \langle \rho \rangle$ in Eq. (7a). However, in forming an approximation, it is advantageous to use our knowledge of how the approximated quantity is to be utilized in subsequent calculations so that as much numerical accuracy as possible is retained while greatly simplifying the analysis. Since we are interested in electron exchange, consider the average radial extent $\langle r \rangle$ of a $3d$ electron:

$$\langle r \rangle = \int_0^\infty r^2 dr R^*(r) r R(r).$$

It follows easily from relations (5) and (6), that:

$$\frac{\langle r \rangle^{-1} d\langle r \rangle}{dP} = \left(7 - \frac{\langle \rho^2 \rangle}{\langle \rho \rangle} \right) \Omega^{-1} \frac{d\Omega}{dP}. \quad (7b)$$

Since we also have

$$\frac{d\langle r \rangle}{dP} = 2 \int r^2 dr R^* r R \left(\frac{1}{R} \frac{\partial R}{\partial P} \right), \quad (7c)$$

a reasonable approximation is to set

$$\frac{(1/R) \partial R}{\partial P} \approx \left(\frac{1}{2} \right) \left(7 - \frac{\langle \rho^2 \rangle}{\langle \rho \rangle} \right) \frac{d\Omega}{dP}. \quad (7d)$$

The difference between (7d) and (7a) is that $\langle \rho^2 \rangle / \langle \rho \rangle$ is used instead of $\langle \rho \rangle$. The achievement is a somewhat better numerical accuracy in the measure of the radial extent of an electron cloud which is a significant consideration for exchange problems.

For sufficiently well separated ions, let us continue with the emphasis on the radial contributions to Eq. (4). In particular, consider next the approximation

$$\vec{r}_j \cdot \nabla \phi \approx \frac{r_j \partial \phi}{\partial r} \approx \frac{\rho_c \partial R}{\partial \rho}, \quad (8)$$

where $\rho_c = 2Zc/3a_0$, and c is the distance between the ions. With Eqs. (5) and (6), Eq. (8) can be written approximately as

$$\vec{r}_j \cdot \nabla \phi \approx (2 \langle \rho_c / \rho \rangle - \frac{1}{2} \rho_c \Omega) R. \quad (9)$$

Setting $f=g$ and using relations (7c) and (9) in expression (4) yields

$$\frac{1}{J} \frac{dJ}{dP} \approx \frac{1}{3} \left(1 + \rho_c - 4 \left\langle \frac{\rho_c}{\rho} \right\rangle \right) \kappa + 2 \left(7 - \frac{\langle \rho^2 \rangle}{\langle \rho \rangle} \right) \frac{d\Omega}{dP} + \frac{d\Lambda}{dP} \quad (10)$$

Equation (10) estimates the variation of the exchange parameter J for $3d$ electrons. To the same approximation, this relation can be determined as easily for the configurations $nl=1s, 2p, 3d, 4f, \dots$; i.e., $l=n-1$. For these electrons,

$$\frac{1}{J} \frac{dJ}{dP} \approx \frac{1}{3} \left(1 + \rho_c - 4 \left\langle \frac{\rho_c}{\rho} \right\rangle \right) \kappa + 2 \left(2n+1 - \frac{\langle \rho^2 \rangle}{\langle \rho \rangle} \right) \frac{d\Omega}{dP} + \frac{d\Lambda}{dP}, \quad (11)$$

where now we must use

$$\rho_c = 2Zc/na_0. \quad (12)$$

The average values in Eq. (11) are computed, of course, as expectation values in the state nl .

Equation (11) involves both a magnitude and an algebraic sign for the relative shift of an exchange integral. The approximations involved to obtain this result are rather rough, but they have been selected in a manner which attempts to preserve the order of magnitude of the most important contributing factors. Hence, the order of magnitude predicted by Eq. (11) should be correct. The terms of Eq. (11) represent the contributions of three different effects. Since each term is subject to the same approximations, a necessary condition for the preservation of the relative contribution of each term to the shift, and hence the algebraic sign of the shift, is met. It is seen in the following sections that the separate contributions of the terms are qualitatively reasonable also.

III. APPLICATIONS

In this section, the application of the results of Sec. II is considered for each of the three cases noted in Sec. I. A very simple example is the direct application to the variation of a magnetic phase boundary which can be discussed as a change in the critical temperature T_c . In mean-field theories of magnetic systems with Heisenberg exchange, it is well known that the Curie temperature is directly proportional to an exchange integral. One thus finds immediately that

$$\frac{1}{T_c} \frac{dT_c}{dP} = \frac{1}{J} \frac{dJ}{dP}. \quad (13)$$

Even in the case of nonordering, singlet ground state systems, exchange interactions can occur,

yielding an observably^{6,7} enhanced Van Vleck susceptibility. One general representation¹⁴ of an enhanced susceptibility is given by the relation

$$\chi_m = \chi / (1 - \lambda\chi), \quad (14)$$

where χ is the unenhanced susceptibility and λ is a constant proportional to J . In Ref. 6, an enhancement of 25% ($\lambda\chi \sim \frac{1}{5}$) has been noted at $P=0$, for cases of Van Vleck susceptibility, so enhancement can be quite significant. From Eq. (14), it is seen that the enhanced susceptibility has a pressure variation given by

$$\frac{1}{\chi_m} \frac{d\chi_m}{dP} = (1 + \lambda\chi_m) \frac{1}{\chi} \frac{d\chi}{dP} + \lambda\chi_m \frac{1}{J} \frac{dJ}{dP}. \quad (15)$$

The first term on the right-hand side in Eq. (15) gives the contribution due to a change in the unenhanced susceptibility which can be found in terms of crystal field parameters, the compressibility, and the scaling parameters. A discussion of this term has been given for a special case in Ref. 9. The second term in Eq. (15) is the contribution due to exchange, and this term is given by Eq. (11).

The special case discussed in Ref. 9 is applicable to the enhanced Van Vleck susceptibility of PrSb. Insofar as the available data permits, consider the pressure dependence for this problem according to Eq. (15). The pressure variation of the unenhanced susceptibility can be written⁹

$$\frac{(1/\chi)d\chi}{dP} \approx - \frac{[5 + 2(1+x)\Delta_0/\Delta]\kappa}{3} - \frac{d\Lambda}{dP} + \frac{[3 + 2(1+x)\Delta_0/\Delta]d\Omega}{dP},$$

where x , Δ_0 , and Δ are $P=0$ crystal-field parameters whose values for PrSb are⁶ $x = -0.966$, $\Delta_0/\Delta = 5.25$. For the praseodymium ion, $\rho_c \sim 6$ and $\langle 1/\rho \rangle \sim \frac{1}{8}$. With $\lambda\chi_m \approx 0.2$ and $\kappa = 1.96 \times 10^{-3} \text{ kbar}^{-1}$, Eq. (15) gives

$$\frac{(1/\chi_m)d\chi_m}{dP} \approx - 3.7 \times 10^{-3} \text{ kbar}^{-1} - \frac{d\Lambda}{dP} + \frac{3.6d\Omega}{dP}.$$

The observed⁶ value is $7 \times 10^{-3} \text{ kbar}^{-1}$. Taking $-d\Lambda/dP \sim d\Omega/dP > 0$, we estimate $d\Omega/dP \sim 2 \times 10^{-3} \text{ kbar}^{-1}$.

As a third example, the occurrence of exchange variation in the optical spectra of $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ is considered for which case sufficient experimental information is already available so that theoretical numerical results can be obtained. Evaluation of the numbers $d\Lambda/dP$ and $d\Omega/dP$ has been accomplished previously¹² for ruby by considering the single ion optical spectra of the Cr^{3+} ions in Al_2O_3 . Consequently, the order of magnitude of the pressure variations of the exchange interactions of pairs of Cr^{3+} ions can be estimated using

TABLE I. Estimated pressure variations of the exchange interactions between first through fourth-nearest-neighbor Cr^{3+} ions in ruby. c is the interionic distance and J is the exchange parameter at zero pressure, both of which are taken from Ref. 19. dJ/dP is estimated using Eq. (10) with $\kappa = 3.9 \times 10^{-4} \text{ kbar}^{-1}$ (Refs. 15-17, 21, 22) $d\Lambda/dP = 4.5 \times 10^{-5} \text{ kbar}^{-1}$, and $d\Omega/dP = 1.5 \times 10^{-5} \text{ kbar}^{-1}$ (Ref. 12).

Neighbors	c (Å)	$J (P=0)$ (cm^{-1})	$\frac{dJ}{dP}$ calc ($\text{cm}^{-1}/\text{kbar}$)
First	2.7	240	0. 2
Second	2.8	84	0. 07
Third	3.2	12	0. 01
Fourth	3.5	-7	-0.007

relation (10) for $3d$ electrons. It is assumed, here, that the screening experienced by the exchange coupled ion pair can be taken to be the same as that found for the interaction of an ion with the crystal field.

Note that a distance dependence is contained in Eq. (10) via the $P=0$ value of J , as well as in ρ_c . Hence, if exchange parameters are known for nearest neighbors, next nearest neighbors, and so forth, estimates of the pressure dependence for each case can be made.

For nearest-neighbor Cr^{3+} ions in ruby, $Z \approx 3$ and $c/a_0 \approx 5.4$, so $\rho_c \approx 11$. Powell and DiBartolo¹⁹ have tabulated the neighbor distances and exchange parameters through fourth-nearest neighbors. Their values are used with Eq. (10) to construct Table I. For this estimate, the expectation values in Eq. (10) are taken from Ref. 18 for hydrogenlike ions.

At the present time, there are no published reports on dJ/dP values for ruby. However, the author is informed²⁰ that an experiment which should provide this information is expected to be completed sometime in the not too distant future.

According to Table I, exchange variations in ruby are expected to be observable with the qualitative result that the exchange magnitude increases. This is a reasonable result since one expects exchange to increase as the amount of overlap increases. Under hydrostatic pressure, the ions are moved together. However, it was noted in Sec. I that the ionic electron cloud is contracted which tends to decrease the overlap. If we consider the ratio $\langle r \rangle / a$, where a is a cell dimension or the ion-to-point charge distance, we find, for ruby, $(a/\langle r \rangle) d(\langle r \rangle / a) / dP \approx -d\Omega/dP + \frac{1}{3}\kappa > 0$. Hence, the Cr^{3+} electron cloud occupies a larger portion of the unit cell producing a larger overlap, a result consistent with Table I.

IV. CONCLUSION

A prototype exchange integral is used in Sec. II for the purpose of estimating the effect of hydrostatic pressure on exchange parameters. The pressure dependence is determined according to a representation of the application of hydrostatic pressure in which the compressibility κ and two scaling parameters Λ (associated with electronic screening) and Ω (associated with wave-function distortion), are used.

The most significant feature of the present work is that it provides, by Eq. (11), an estimate of the relative contributions of κ , Λ , and Ω to the hydrostatic pressure dependence of exchange for electrons in the $n, l = n - 1$ configurations. A second feature, seen in Sec. III, is that the present theory shows explicitly that electronic screening and wave-function distortion tend to compete against the variations due to the compressibility of the solid. Qualitatively, we find, quite reasonably, that moving the ions closer together enhances exchange while contracting the electron clouds¹³ on the ions reduces the exchange.

Section III illustrates the application of the present work by considering the variations of magnetic critical temperatures, exchange enhanced susceptibility, and, in greater detail, the exchange interactions of pairs of Cr^{3+} ions in ruby. The reason for using the ruby example is twofold. First, a successful analysis of the pressure dependence of the single-ion Cr^{3+} spectra has been performed previously¹² using the scaling theory. Second, the prospects²⁰ of the availability of measured dJ/dP values in the near future are good.

The estimated values of dJ/dP for ruby, given in Table I are sufficiently large that they should be observable at low temperatures and high pressures. Qualitatively, any changes in the ruby exchange parameters are expected to be in the direction of increasing magnitude with increasing pressure.

It should also be noted that ruby is a relatively stiff substance. Materials with larger compressibilities may have more readily observable exchange variations than those of ruby, depending on the competition between the effects of compressibility and the changes of the wave function.

A virtue of the scaling hypothesis is that it can easily be incorporated into whatever formalism is being used. The present work, on exchange, plus the results of Refs. 9 and 12, concerned with crystal-field theory, can be used to provide a common parametrization of the pressure variations of a variety of phenomena; e.g., the pair lines in ruby must experience a shift under pressure that is due to the combined effects of changes

in both the crystal-field parameters and the exchange parameters.

Of course, the final judgment of the utility of the scaling hypothesis must be determined by how well it agrees with experimental observations. Section III discusses several applications. The results of that section can be considered as providing addi-

tional means by which the theory following from the scaling hypothesis can be examined.

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- ¹C. E. Weir, E. R. Lippincott, A. Van Valkenburg, and E. N. Bunting, *J. Res. Natl. Bur. Stand. A* **63**, 55 (1959).
- ²J. D. Barnett, S. Block, and G. J. Piermarini, *Rev. Sci. Instrum.* **44**, 1 (1973).
- ³R. A. Forman, G. J. Piermarini, J. D. Barnett, and S. Block, *Science* **176**, 284 (1972).
- ⁴G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, *J. Appl. Phys.* **46**, 2774 (1975).
- ⁵R. A. Forman, B. A. Weinstein, and G. J. Piermarini, *Colloques Internationaux du Centre National de la Recherche Scientifique*, Lyon, No. 255, p. 51, 1976 (unpublished).
- ⁶R. P. Guertin, J. E. Crow, L. D. Longinotti, E. Bucher, L. Kupferberg, and S. Foner, *Phys. Rev. B* **12**, 1005 (1975).
- ⁷F. P. Missell, R. P. Guertin, and S. Foner, *Bull. Am. Phys. Soc.* **22**, 427 (1977).
- ⁸H. T. Weaver and J. E. Schirber, *AIP Conf. Proc.* **24**, 49 (1975).
- ⁹R. G. Munro, *Phys. Lett. A* (to be published).
- ¹⁰D. E. McCumber and M. D. Sturge, *J. Appl. Phys.* **34**, 1682 (1963).
- ¹¹T. Muramoto and T. Hashi, *Phys. Lett. A* **51**, 423 (1975).
- ¹²R. G. Munro, *J. Chem. Phys.* **67**, 3146 (1977).
- ¹³In the case of ruby, $d\Omega/dP > 0$, and since the site symmetry is unchanged, wave-function distortion occurs as a contraction of the electron cloud.
- ¹⁴B. R. Cooper and O. Vogt, *Phys. Rev. B* **1**, 1218 (1970).
- ¹⁵D. Schiferl, H. d'Amour, W. Denner, H. Schulz, and W. B. Holzapfel (unpublished).
- ¹⁶D. Schiferl and J. C. Jamieson (unpublished).
- ¹⁷Y. Sato and S. Aikimoto (unpublished).
- ¹⁸E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge U. P., Cambridge, England, 1967).
- ¹⁹R. C. Powell and B. DiBartolo, *Phys. Status Solidi A* **10**, 315 (1972).
- ²⁰R. A. Forman (personal communication).
- ²¹P. W. Bridgman, *Proc. Am. Acad. Arts. Sci.* **77**, 189 (1949).
- ²²H. V. Hart and H. G. Drickamer, *J. Chem. Phys.* **43**, 2265 (1965).