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Core Polarization in Cr^{53}†

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Theoretical and experimental values for the contribution of core polarization to the hyperfine structure of excited states of Cr^{53} are compared. A theory is developed for extracting the core contributions to the magnetic field from the measured hyperfine constants. It is necessary to take account of configuration interaction with an actual configuration of unpaired *s* electrons. A value of −525 000 G is deduced for the magnetic field at the nucleus produced by core polarization. The minus sign indicates that this field is antiparallel to the net spin of the atom. This is compared with theory and with the results of other experiments. Corrections due to relativity, the second-order Zeeman effect, and the breakdown of *LS* coupling are considered.

INTRODUCTION

It was shown by Abragam, Horowitz, and Pryce[1] that the magnetic field at the nucleus that was responsible for hyperfine structure in the ground states of vanadium, manganese, and cobalt was a sum of two fields. The first field is the one to be expected from the orbital and spin motion of valence *d* electrons. They attributed the second field to the admixture of configurations containing unpaired *s* electrons. Such configurations are important because the unpaired *d* electrons all have their spins in the same direction to produce the state of highest multiplicity according to Hund's rule. The *s* electron, whose spin is in the same direction as the majority of *d*'s, experiences an exchange interaction and is raised to an unfilled *s* orbit. Even a small admixture of this excited configuration can produce a large magnetic field because of the Fermi contact term of the inner unpaired *s* electron. This effect is called core polarization.

As a result of the first Mössbauer work, it was discovered that the magnetic field at the iron nucleus was of the right magnitude but opposite in direction to that anticipated. Two sets of authors[2,3] showed that core polarization could qualitatively explain this result although the quantitative agreement was unsatisfactory. One set of authors, Watson and Freeman,[4] went on to give a systematic theoretical treatment to the general problem of core polarization in the first-row transition elements as well as a summary of experimental observations. They found that each *d* electron in a divalent ion should contribute a magnetic field at the nucleus of approximately 115 000 G and that each *d* electron in the $(3d)^n(4s)^2$ ground state of free atoms should contribute a field of about 23 000 G.

This rather remarkable description of a field per unit spin was in good agreement with experimental results for the divalent ions, but the agreement was poor for the free atoms. The two species differ only in the absence or presence of the $(4s)^2$ electrons which lie entirely outside the $3d$ shell. It would appear that theory and experiment agree when the excited electrons are core electrons in the sense that they lie within or at most overlap with the polarizing *d* shell. Recently it has been shown[5] that the latest experimental results for the polarization fields in free atoms are in better agreement with the calculated fields than were earlier measurements. However, the field values deduced from observations are small, and those predicted by theory are the result of cancellations between much larger fields. Thus the field per unit spin in the ion is almost entirely quenched by the addition of the $4s$ electrons as can be seen from the figures quoted above.

Chromium is particularly suitable for testing the above hypothesis. Unique among the first-row transition elements, its ground configuration is $(3d)^5 4s$. An excited configuration $(3d)^5 4p$ is connected to the ground state by an intense optical resonance line in the visible range and can therefore be investigated by double-resonance techniques. The magnetic field at the nucleus for the $(3d)^5 4p$ configuration should arise entirely from the *p* electron since the half-filled *d* shell couples to a spherically symmetric $^6S_{5/2}$ ground state. Core-polarization contributions to the magnetic field can then be studied against the relatively smaller field due to the *p* electron. In this way one may verify the core-polarization theory for a free atom in the favorable electronic environment normally associated with the ion.

EVALUATION OF THE HYPERFINE-STRUCTURE CONSTANTS

A comparison between theoretical and experimental values for the magnetic field produced by core polarization is most conveniently made through the magnetic

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[1] A. Abragam, J. Horowitz, and M. H. L. Pryce, Proc. Roy. Soc. (London) **A230**, 169 (1955).

[2] D. A. Goodings and V. Heine, Phys. Rev. Letters **5**, 370 (1960).

[3] A. J. Freeman and R. E. Watson, Phys. Rev. Letters **5**, 498 (1960).

[4] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).

[5] R. Winkler, Z. Physik **184**, 433 (1965).

hyperfine constant $a_c^{(1)}$ given by

$$a_c=\tfrac{4}{3}(\mu_N/I)\mu_0\mathcal{X}\,, \qquad (1)$$

where μ_N is the nuclear moment (-0.4735 nm in the case of Cr^{53}), $I=\frac{3}{2}$ is the nuclear spin, and $\mathcal{X}$ is the magnetic field produced by the electrons expressed in atomic units ($e=m=\hbar=1$). A value for the magnetic field $\mathcal{X}$ is obtained from the observed hyperfine splittings with the aid of the theory developed below. The experimental data consist of values for the hyperfine constants a for each of the J levels of the excited ${}^7P$ term.[6] Contributions of the electronic structure by whatever mechanism to the magnetic field are reflected as corresponding contributions to the a value.

For the case of equivalent electrons discussed by Abragam *et al.*,[1] the a value is expressed as a linear combination of the a value to be expected from the orbital and spin motions of the electron calculated in *LS* coupling and an a value due entirely to core polarization. For nonequivalent electrons there is the additional problem of decoupling the electron shells as discussed by Trees.[7] This may be done by straightforward application of decoupling formulas,[8] or in the following manner. The wave function in the *LSJ* representation is transformed to the j_1j_2J scheme where j_1 and j_2 are the possible j values for the unfilled shells. For $d^5p\ {}^7P$ this is especially simple since $j_1=\frac{5}{2}$ and $j_2=\frac{1}{2}$ or $\frac{3}{2}$. The j_1j_2JM basis is then replaced by the completely uncoupled $j_1m_1j_2m_2$ basis, and the a values calculated from the definition,[9]

$$A=(JJ|T_e^{(1)}|JJ)(II|T_n^{(1)}|II)\,,$$

where the first matrix element is that of a first-order tensor operator in the state of highest M_J, and the second is just the nuclear magnetic moment. It is assumed that $T_e^{(1)}$ is the sum of operators that act upon the different shells independently. To illustrate the simplicity of this approach we have

$$\begin{aligned}|(d^5p)^7P_4,4\rangle&=|(d^5)^6S_{5/2}(p)^2P_{3/2}\,4,4\rangle\\&=|{}^6S_{5/2}\,\tfrac{5}{2}\,{}^2P_{3/2}\,\tfrac{3}{2}\rangle\end{aligned} \qquad (2)$$

for the transformation of the state of highest J. Then

$$\begin{aligned}&\langle{}^7P_4\,4|T_e^{(1)}|{}^7P_4\,4\rangle\\&\quad=\langle{}^6S_{5/2}\,\tfrac{5}{2}\,{}^2P_{3/2}\,\tfrac{3}{2}|T_e^{(1)}(d)+T_e^{(1)}(p)|{}^6S_{5/2}\,\tfrac{5}{2}\,{}^2P_{3/2}\,\tfrac{3}{2}\rangle\\&\quad=\langle{}^6S_{5/2}\,\tfrac{5}{2}|T_e^{(1)}(d)|{}^6S_{5/2}\,\tfrac{5}{2}\rangle+\langle{}^2P_{3/2}\,\tfrac{3}{2}|T_e^{(1)}(p)|{}^2P_{3/2}\,\tfrac{3}{2}\rangle\end{aligned}$$

or

$$A({}^7P_4)=A({}^6S_{5/2})+A({}^2P_{3/2})=A({}^2P_{3/2})\,, \qquad (3)$$

since $A({}^6S_{5/2})$ vanishes for the half-filled d shell. Since $A=aIJ$, Eq. (3) becomes

$$a({}^7P_4)=\tfrac{5}{8}a({}^6S_{5/2})+\tfrac{3}{8}a({}^2P_{3/2})=\tfrac{3}{8}a({}^2P_{3/2})\,, \qquad (4)$$

and thus the measured a values are related to the single-electron contributions.

The above method has two additional advantages. First, it enables one to relate the contributions of the different shells to their uncoupled angular momenta. This is essential in order to include the core polarization. By analogy with Abragam *et al.*, we replace $a({}^6S_{5/2})$ by $a'({}^6S_{5/2})+a_c$, where $a'({}^6S_{5/2})$ is the spin and orbit contribution, zero in this case, and a_c is the core term.[10] Thus Eq. (4) can be written

$$a({}^7P_4)=\tfrac{5}{8}a_c+\tfrac{3}{8}a_{3/2}\,, \qquad (5)$$

where a further simplification in notation has been introduced. The second advantage is the explicit appearance of off-diagonal matrix elements which occur, for example, in the calculation of $a({}^7P_3)$. In this case

$$\begin{aligned}|{}^7P_3\,3\rangle=\tfrac{2}{3}|{}^6S_{5/2}\,\tfrac{5}{2}\,{}^2P_{1/2}\,\tfrac{1}{2}\rangle-\frac{5\sqrt{2}}{12}|{}^6S_{5/2}\,\tfrac{5}{2}\,{}^2P_{3/2}\,\tfrac{1}{2}\rangle\\+\frac{(\sqrt{30})}{12}|{}^6S_{5/2}\,\tfrac{3}{2}\,{}^2P_{3/2}\,\tfrac{3}{2}\rangle,\end{aligned}$$

and the hyperfine operator connects the states represented by the first two wave functions. Such matrix elements may be evaluated by use of formulas in Lurio, Mandel, and Novick,[11] and are distinguishable by the presence of a factor ξ which is defined by Schwartz.[9] In this way one arrives at the following set of equations:

$$\begin{aligned}a({}^7P_4)&=\tfrac{5}{8}a_c+\tfrac{3}{8}a_{3/2}\,,\\a({}^7P_3)&=\frac{55}{72}a_c+\frac{2}{27}a_{1/2}+\frac{35}{216}a_{3/2}+\frac{25}{216}\xi a_{3/2}\,,\\a({}^7P_2)&=\frac{10}{9}a_c-\frac{7}{54}a_{1/2}+\frac{3}{162}a_{3/2}+\frac{105}{648}\xi a_{3/2}\,.\end{aligned} \qquad (6)$$

The measured values of the interaction constants are reported in the preceding paper.[6] They are

$$\begin{aligned}|a({}^7P_4)|&=11.6\ \mathrm{Mc/sec}\,,\\|a({}^7P_3)|&=0\ \mathrm{Mc/sec}\,,\\|a({}^7P_2)|&=26.2\ \mathrm{Mc/sec}\,.\end{aligned}$$

As pointed out in the same paper, the result is entirely inconsistent with a theory of hfs which ascribes the splitting to the interaction of μ_I with only the magnetic field produced by the outer p electron. Under the assumption that only the p electron makes a contribution, the magnetic interaction constants are expected to be in the ratio $|a(4)|:|a(3)|:|a(2)|=81:140:101$. The

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[6] H. Bucka, B. Budick, R. J. Goshen, and S. Marcus, preceding paper, Phys. Rev. **144**, 96 (1966).

[7] R. E. Trees, Phys. Rev. **92**, 308 (1953).

[8] G. Racah, Phys. Rev. **62**, 438 (1942), Eqs. (44).

[9] C. Schwartz, Phys. Rev. **97**, 380 (1955).

[10] The core contribution includes a factor g_J-1 which is the projection of S on J consistent with the assumptions of the core-polarization mechanism. For $(d^5)^6S_{5/2}$, $S=J$, and the projection becomes -1.

[11] A. Lurio, M. Mandel, and R. Novick, Phys. Rev. **126**, 1758 (1962).

above equations indicate that the observed quenching of the hfs in the $J=3$ level is explained at least qualitatively by the theory including core polarization.

To get a soluble, in fact overdetermined, set of equations, one can make the substitutions $\xi=1$ and $a_{1/2}=5a_{3/2}$. The last assumption implies the neglect of relativistic effects (discussed below) and of core-polarization effects of the p electron. The equations are not consistent. The situation is not improved by inclusion of the core polarization for the p electron according to the simple theory of Goodings.[12] A satisfactory explanation must be sought in another direction.

CONFIGURATION-INTERACTION EFFECTS ON HYPERFINE STRUCTURE

In presenting the theory for the hyperfine structure of the d^5p configuration in chromium, we have sought to include that particular form of configuration interaction called core polarization. Under this title we refer to the admixture of configurations of unpaired s electrons produced by an exchange interaction with the valence d electrons. Moreover, there exists an overlapping configuration $(3d)^4 4s4p$ with states of identical angular momentum to those of d^5p and an actual unpaired s electron. Results of measurements on these states are reported in the preceding paper.[6] The question arises as to the admixture of this nearby configuration.

This problem has been dealt with successfully by Rosenzweig.[13] He shows that the matrix element of the Coulomb operator connecting the ^7P terms of the two configurations can be written as

$$-\sqrt{2}\left[\tfrac{1}{5}R^2(sp,dp)-\tfrac{1}{3}R^1(sp,pd)\right],$$

where $R^1(sp,pd)$ and $R^2(sp,dp)$ are Slater integrals defined by Condon and Shortley.[14] Configuration interaction of this type is also important in explaining gross features of atomic spectra such as shifts in the energy levels. Values for the above integrals have been deduced by Racah and his co-workers by means of a least-squares fit to the energy levels of Ti II and Cu II. By interpolation one obtains $\frac{1}{5}R^2=1480$ cm^{-1} and $\frac{1}{3}R^1=3510$ cm^{-1} for Cr II.[15] The value of this matrix element is not expected to change much in going to the first spectrum and is to be compared with the separation of the two terms of the two configurations, $\Delta=4432$ cm^{-1}. The matrix element given above and the measured separation are sufficient to describe the configuration admixture. By diagonalization of the 2×2 submatrix for the two configurations,

$$\begin{aligned}\Psi(d^5p)&=(0.806)^{1/2}\Psi(d^5p)+(0.194)^{1/2}\Psi(d^4sp)\,,\\ \Psi(d^4sp)&=(0.194)^{1/2}\Psi(d^5p)-(0.806)^{1/2}\Psi(d^4sp)\,.\end{aligned}\tag{7}$$

The previously derived Eqs. (6) for the hyperfine constants must be modified by including the a values for the d^4sp configuration. These are calculated by the method outlined above. The fact that we are dealing with the state of highest multiplicity narrows the choice of terms for each shell to ^5D, ^2S, and ^2P, respectively. In addition to the off-diagonal matrix elements mentioned above, we will encounter matrix elements of the type $(^5D_4\,3|T_e^{(1)}|^5D_3\,3)$. These can be related to the on-diagonal matrix elements via the reduced matrix elements. The entire a value can be written as a linear combination of $a(^5D_4)$, $a(^5D_3)$, $a(^5D_2)$, $a(^5D_1)$, $a(^2S_{1/2})$, $a(^2P_{1/2})$, $a(^2P_{3/2})$, $\xi a(^2P_{3/2})$, and a_d, where a_d is the core polarization produced by four d electrons. The first four quantities can be related to one another and written in terms of

$$a(^5D_4)=(8/7)g_I\mu_0\langle 1/r^3\rangle 3d.$$

We then make use of the coefficients in Eqs. (7) to arrive at a final set of equations relating measured quantities to single-electron and core-polarization a values:

$$\begin{aligned}a(d^5p\ {}^7P_4)=0.806(\tfrac{5}{8}a_c+\tfrac{3}{8}a_{3/2})\\ +0.194\Bigg[0.775\frac{8}{7}g_I\mu_0\left\langle\frac{1}{r^3}\right\rangle_{3d}\\ +0.109a_s-0.056a_{3/2}+0.820a_d\Bigg]\,,\end{aligned}\tag{8a}$$

$$\begin{aligned}a(d^5p\ {}^7P_3)=0.806\left(\frac{55}{72}a_c+\frac{35}{54}a_{3/2}\right)\\ +0.194\Bigg[0.743\frac{8}{7}g_I\mu_0\left\langle\frac{1}{r^3}\right\rangle_{3d}\\ +0.106a_s+0.145a_{3/2}+1.006a_d\Bigg]\,,\end{aligned}\tag{8b}$$

$$\begin{aligned}a(d^5p\ {}^7P_2)=0.806\left(\frac{10}{9}a_c-\frac{101}{216}a_{3/2}\right)\\ +0.194\Bigg[0.491\frac{8}{7}g_I\mu_0\left\langle\frac{1}{r^3}\right\rangle_{3d}\\ +0.112a_s+0.390a_{3/2}+0.795a_d\Bigg]\,,\end{aligned}\tag{8c}$$

$$\begin{aligned}a(d^4sp\ {}^7P_3)=0.194\left(\frac{55}{72}a_c+\frac{35}{54}a_{3/2}\right)\\ +0.806\Bigg[0.743\frac{8}{7}g_I\mu_0\left\langle\frac{1}{r^3}\right\rangle_{3d}\\ +0.106a_s+0.145a_{3/2}+1.006a_d\Bigg]\,,\end{aligned}\tag{8d}$$

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[12] D. A. Goodings, Phys. Rev. **123**, 1706 (1961).

[13] N. Rosenzweig, Phys. Rev. **88**, 580 (1952).

[14] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1957).

[15] Z. Goldschmidt (private communication).

where $|a(d^5p\ {}^7P_4)|=11.6$ Mc/sec, $|a(d^5p\ {}^7P_3)|=0$, $|a(d^5p\ {}^7P_2)|=26.2$, and $|a(d^4sp\ {}^7P_3)|=70.4$. In the expressions for each configuration we have substituted $\xi=1$ and $a_{1/2}=5a_{3/2}$. The coefficients of a_d have been derived by writing $a({}^5D_4)=a'({}^5D_4)+a_d$, $a({}^5D_3)=a'({}^5D_3)+a_d$, where the term in a_d is independent of J since as noted above[10] the J dependence is contained in the factor g_J-1, and g_J is independent of J for ${}^5D$.[16]

One may further reduce Eq. (8) to four equations in four unknowns by substituting $3.25(1/a_0^3)$ for $\langle 1/r^3\rangle_{3d}$.[17] Then the equations can be solved for various choices of signs of the measured hyperfine constants. The only choice of signs which gives a plausible result for a_c and $a_{3/2}$ is plus for $a(d^5p\ {}^7P_2)$ and minus for the other measured a values. With this choice the values of

$$a_c=+45.5 \text{ Mc/sec}$$

and

$$a_{3/2}=-19.7 \text{ Mc/sec}$$

are deduced. These compare well with the results obtained in the next section and with the Watson and Freeman prediction[4] discussed in a later section. These quantities were found to be relatively independent of the coefficients of a_d within the limits of their uncertainties.[16] The values obtained for a_d and a_s, however, are extremely sensitive to any change in the coefficients of a_d. Thus it is not surprising that the computed values of $a_s=+3875$ Mc/sec and $a_d=-656$ Mc/sec are much larger than the values one might expect and opposite in sign. However, with a change in the coefficient of a_d in Eq. (8c) from 0.795 to 0.745, within its 10% uncertainty, the following solutions are obtained:

$$\begin{aligned} a_c&=51.4 \text{ Mc/sec},\\ a_{3/2}&=-26.2 \text{ Mc/sec},\\ a_d&=17 \text{ Mc/sec},\\ a_s&=-654 \text{ Mc/sec}. \end{aligned}$$

While a_c and $a_{3/2}$ are not greatly changed, a_d and a_s are considerably altered, and all four values are close to those expected.

EXTRACTION OF THE CORE POLARIZATION

Since hyperfine-structure measurements have been made in the $J=3$ states of both configurations, one can solve for the core-polarization contribution to be expected from the d^5p configuration alone by making use of Eqs. (8b) and (8d). This method is free from errors in the calculation of $a(d^4sp)$, from ambiguities in the coefficients of a_d, and from uncertainty in the value of $\langle 1/r^3\rangle_{3d}$. It also avoids the arbitrary choice of sign for the measured a values except in Eq. (8d) where the large contribution of a_s makes the negative sign most likely. In this way one obtains

$$22.3=\frac{55}{72}a_c+\frac{35}{54}a_{3/2}. \tag{9}$$

An estimate for $a_{3/2}$ can be made from the fine-structure constant ζ_{4p} by use of the formula[7]

$$a_p=0.545[\zeta_{4p}/\lambda(l,Z)Z_i]g_I\times10^{-3}, \tag{10}$$

where ζ_{4p} is in wave numbers, $\lambda(l,Z)=1.0094$ is a relativistic correction tabulated by Kopfermann,[18] $Z_i=Z-4$ for p electrons, and g_I is the nuclear g factor. One can evaluate ζ_{4p} from the known fine structure of the ${}^7P$ multiplet since $\zeta({}^7P)=\frac{1}{6}\zeta_{4p}$ and $4\zeta({}^7P)=112$ cm^{-1} (interval rule obeyed). Thus, $\zeta_{4p}=168$ cm^{-1}. This result is consistent with a value of 260 cm^{-1} for ζ_{4p} which has been determined from fine and hyperfine-structure measurements in the d^5sp configuration of Mn.[19] From Eq. (10) a_p may be evaluated and is found to be -43.0 Mc/sec. Then

$$a_{3/2}=a_p(8/15)F_r(\tfrac{3}{2},Z_i), \tag{11}$$

where $F_r(\frac{3}{2},Z_i)$ is another relativistic correction factor tabulated by Kopfermann. Thus, $a_{3/2}=-23.1$ Mc/sec. We return to Eq. (9) and compute a_c. We find $a_c=+48.7$ Mc/sec.

ZEEMAN, RELATIVISTIC, AND INTERMEDIATE-COUPLING CORRECTIONS

The a values measured in the $3d^54p$ configuration upon which much of the foregoing analysis has been based are either small or zero. It is therefore necessary to consider other effects which may possibly contribute to the hyperfine constants.

A. Magnetic-Field Effects

In second-order perturbation theory the magnetic-field operator connects states of different J but the same M_J. This results in a shift of the Zeeman levels proportional to $(\mu_0H)^2$. In evaluating the hyperfine constants (see Ref. 6), we equate the transition frequency $h\nu$ to the difference in energy of the two resonating Zeeman levels. The second-order shifts will most likely be different for the two levels and will hence appear as a contribution to a. It can be shown[20] that the contribution of such an effect to the transition frequency

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[16] The factors relating $a'({}^5D_4)$ to $a'({}^5D_3)$ have therefore not been applied to the coefficients of a_d in reducing the derived linear combination to fewer parameters. Some ambiguity exists in the method of evaluating these coefficients since the off-diagonal matrix elements of the hyperfine operator can be written as proportional to $a({}^5D_J)$ or to $a({}^5D_{J-1})$. However, this ambiguity produces an uncertainty of at most 4%, 11%, and 10% for $J=4$, $J=3$, and $J=2$, respectively.

[17] R. E. Watson (private communication).

[18] H. Kopfermann, *Nuclear Moments* (Academic Press Inc., New York, 1958).

[19] G. Nöldecke, Z. Physik **153**, 164 (1958).

[20] R. J. Goshen, Ph.D. dissertation, Columbia University, 1964 (unpublished).

can be written as

$$\Delta\nu=\frac{K(J)[P(J,M_J)-P(J,M_{J-1})](\mu_0 H)^2}{E_J-E_{J-1}}$$

$$+\text{a term for } J+1\,, \tag{12}$$

where

$$K(J)$$

$$=\frac{(J-L+S)(J+L-S)(J+L+S+1)(L+S+1-J)}{4J^2(2J-1)(2J+1)}$$

and $P(J,M_J)=J^2-M_J^2$. For the shift in frequency of the $|{}^7P_4\,4\rangle\rightarrow|{}^7P_4\,3\rangle$ transition at a typical field of 300 G, we find $\Delta\nu\approx-0.01$ Mc/sec. This is negligible compared to the measured a values.

B. Relativistic Effects

The relativistic corrections alter the ratio $a_{1/2}=5a_{3/2}$ since

$$\begin{aligned} a_{1/2}&=a_p(8/3)F_r(\tfrac{1}{2},Z_i)\,,\\ a_{3/2}&=a_p(8/15)F_r(\tfrac{3}{2},Z_i)\,. \end{aligned} \tag{13}$$

Values for the correction factors taken from Kopfermann are $F_r(\frac{1}{2},20)=1.0404$ and $F_r(\frac{3}{2},20)=1.0084$. Since $a_{1/2}$ enters the expression for $a({}^7P_3)$ in Eq. (6) with the small coefficient 2/27, the small modification in the ratio due to relativity may be neglected. Core polarization produced by the p electron can also alter this ratio. However, no evidence for this effect exists in transition elements, and, even if present, it is very likely quite small. The relativistic contribution of the $3d^5$ electrons to the hyperfine structure has been estimated to be much smaller than the core-polarization contribution.[21]

C. Breakdown of *LS* Coupling

In the preceding paper[6] the breakdown of LS coupling was considered in the light of the presence of intercombination lines and was shown to have a negligible effect on the g_J values to the precision of the measurement. In the Appendix it is shown that the wave functions describing the admixture can be derived by treating the spin-orbit interaction as a perturbation and can be written

$$\begin{aligned} \Psi({}^7P_3)&=0.999\Psi({}^7P_3)+0.041\Psi({}^5P_3)\,,\\ \Psi({}^7P_2)&=0.999\Psi({}^7P_2)+0.037\Psi({}^5P_2)\,, \end{aligned} \tag{14}$$

in good agreement with the empirically derived functions. Thus the hyperfine structure in the ${}^5P_3$ state, itself of the same order of magnitude as in the ${}^7P_3$ state (neglecting configuration interaction), is multiplied by a small coefficient and may be neglected.

TABLE I. Values of experimental hyperfine interaction χ, H_c, and $H_c/\mathcal{S}$ for the divalent ion series in hydrated salts.[a]

Ion	$V^{2+}(3d^3)$	$Mn^{2+}(3d^5)$	$Co^{2+}(3d^7)$	$Cu^{2+}(3d^9)$
χ (a.u.)	-2.8	-3.1	-2.5	-2.9
$H_c/\mathcal{S}$ (kG)	-118	-130	-105	-122
H_c (kG)	-354	-650	-315	-122

[a] This tabulation given by Watson and Freeman (Ref. 4) from χ's reported by Abragam (Ref. 1).

COMPARISON WITH THEORY

The mechanism for core polarization discussed in the Introduction implies a difference in the spin densities, $|\psi_\uparrow(0)|^2-|\psi_\downarrow(0)|^2$, of the inner s electrons with spins in the directions indicated by the arrows. A convenient measure of this effect is given by Watson and Freeman[4] as

$$\chi=\frac{4\pi}{\mathcal{S}}\sum_{s\text{ shells}}[\rho_\uparrow(0)-\rho_\downarrow(0)]\,, \tag{15}$$

where $\mathcal{S}$ denotes the number of unpaired spins and $\rho(0)=|\Psi(0)|^2$. With χ in atomic units (a.u.), $H_c/\mathcal{S}$ is found in gauss by using the conversion factor 1 a.u.$=4.21\times10^4$ G. Values for χ based on an analysis of experimental hyperfine data for ions in hydrated salts are tabulated in Table I together with the contact-term effective field H_c and also with $H_c/\mathcal{S}$ which is the field per unpaired spin. We see that χ has a roughly constant value of about -3 atomic units (a.u.).

The value for a_c reported here can be converted to χ with the help of Eq. (1) when a_c is expressed in millikaisers ($\frac{4}{3}\mu_0=2.12$ in a.u.). Using the value of a_c obtained from Eq. (9), we find $\chi=-2.5$ a.u. in good agreement with the ion values. This corresponds to a magnetic field at the nucleus of $-525\,000$ G due to core polarization.

COMPARISON WITH OTHER EXPERIMENTS

The experiment having the most direct bearing on the present problem is the measurement of Childs *et al.*[22] on the chromium ground state. These authors find $|a({}^7S_3)|=82.5985\pm0.0015$ Mc/sec. The theoretical value is -144 Mc/sec due to the s electron and neglecting core-polarization effects. Their discussion of core polarization is formulated somewhat differently from that given here and does not lead to satisfactory agreement between experimental and predicted values. In terms of the formulation presented here, the ground-state wave function is written

$$|{}^7S_3\,3\rangle=|{}^6S_{5/2}\,\tfrac{5}{2}\,{}^2S_{1/2}\,\tfrac{1}{2}\rangle\,, \tag{16}$$

from which it follows that

$$a({}^7S_3)=\tfrac{5}{6}a_c+\tfrac{1}{6}\,a_s\,, \tag{17}$$

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[21] P. G. H. Sanders (private communication).

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where $|a(^7S_3)| = 82.6$ Mc/sec and $\frac{1}{6}a_s = -144$ Mc/sec. Since the s electron is expected to dominate as in the d^4sp configuration discussed above, we prefer to choose the negative sign for $a(^7S_3)$. Thus $\frac{5}{6}a_c = 61.4$ and $a_c = 73.8$ Mc/sec. This gives a value for χ of -3.7 a.u. The difference from the value found above may be due to an incomplete treatment of configuration interaction, to differences in the core polarization of s and p electrons, or to uncertainties in the values of a_s and a_p.

In contrast to this rough agreement with ion values for χ obtained in the two experiments on the half-filled d shell in chromium, hyperfine measurements on the $(3d)^5 4s4p$ configuration in manganese[19,23] show an almost total lack of core polarization. The combination $5a_c + a_s$ occurs in an analysis of the ^8P term of this configuration (with the addition of a p-electron contribution) just as it does for the chromium ground state. We find

$$\begin{aligned} 5a_c + a_s &= 2230 \text{ Mc/sec for Cr}, \\ 5a_c + a_s &= 3680 \text{ Mc/sec for Mn}, \end{aligned} \tag{18}$$

where the sign and magnitude of the g factors have been scaled to Mn. The theoretical value for a_{4s} is 3700 Mc/sec. Recently Winkler[5] has shown the presence of core polarization in the $(3d)^5 4s4p$ configuration. His treatment is based on the introduction of a "polarization gradient" term which is opposite in sign to the core polarization contribution and which can be evaluated from isotope-shift data. Since no work has been done on the isotope shift in manganese, this new parameter can only be estimated.

SUMMARY

The theory for core polarization proposed to explain the hyperfine structure of transition-metal ions has been shown to be in agreement with experiments performed on excited configurations of free atoms. The interpretation of the experiments is based on the vanishing hyperfine structure in the $^7P_3$ state of the configuration $(3d)^5 4p$ whose configuration interaction with the $^7P_3$ state of the overlapping configuration $(3d)^4 4s4p$ is also taken into account. Hyperfine-structure measurements in states of both configurations permit the extraction of the core polarization produced by the half-filled d shell. A value for χ of -2.5 a.u. is found. The predicted value is about -3 a.u. When the formalism developed here is applied to the chromium ground state, a value for χ of -3.7 a.u. is deduced. This difference probably reflects the neglect of a more complete consideration of configuration interaction, but the agreement is nonetheless encouraging. The chromium results are in marked contrast to the apparent absence of core polarization in the $(3d)^5 4s4p$ configuration in manganese.

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APPENDIX

We consider matrix elements of the spin-orbit operator $\mathcal{H}_{\text{so}} = \sum_i \zeta_i(r) \mathbf{l}_i \cdot \mathbf{s}_i$ between states of the d^5p configuration:

$$\langle d^5(S_1L_1)p(S_2L_2)SLJ| \times \sum_i \zeta_i(r) \mathbf{l}_i \cdot \mathbf{s}_i | d^5(S_1'L_1')p(S_2'L_2')S'L'J\rangle.$$

By the methods of Racah[8] this can be shown to equal

$$(-1)^{S'+L+J} \begin{Bmatrix} S & S' & 1 \\ L' & L & J \end{Bmatrix} [(2S+1)(2S'+1)(2L+1)(2L'+1)]^{1/2}$$

$$\times \Bigg[(-1)^{S_1+S_2+S'+1+L_1+L_2+L'+1} \zeta_d \begin{Bmatrix} S & 1 & S' \\ S_1' & S_2 & S_1 \end{Bmatrix} \begin{Bmatrix} L & 1 & L' \\ L_1' & L_2 & L_1 \end{Bmatrix} [l(l+1)(2l+1)]^{1/2} (d^5S_1L_1 \| V^{11} \| d^5S_1'L_1')$$

$$+ (-1)^{S_1'+S_2'+S+1+L_1'+L_2'+L+1} 3\zeta_p \begin{Bmatrix} S & 1 & S' \\ S_2' & S_1 & S_2 \end{Bmatrix} \begin{Bmatrix} L & 1 & L' \\ L_2' & L_1 & L_2 \end{Bmatrix} \Bigg],$$

where the matrix elements of the double tensor V^{11} have been tabulated by Slater.[24]

The matrix elements of $\mathcal{H}_{\text{so}}$ can now be evaluated between ^7P_J and each of the ^5P_J arising from d^5p. Three such quintet states exist whose parents are ^6S, ^4P, and ^4D of d^5. The appropriate linear combination that corresponds to the lowest ^5P term can be found by diagonalizing the Coulomb operator between these states. This has been done[25] with the aid of matrix elements computed by Ishidzu and Obi[26] using their values for F_2, G_1, and G_3. The off-diagonal matrix elements are small, and the state of lowest energy can be found using perturbation

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theory. In this way, one obtains

$$\Psi({}^5P)=0.995\Psi(d^5\,{}^6S\,p^5P)-0.101\Psi(d^5\,{}^4P\,p^5P)-0.110\Psi(d^5\,{}^4D\,p^5P).$$

Using this function one finds

$$\langle {}^7P_3|\mathcal{H}_{\mathrm{so}}|{}^5P_3\rangle=0.995(\tfrac{1}{3}\sqrt{5})\zeta_p+0.1(10/3)^{1/2}\zeta_d,$$
$$\langle {}^7P_2|\mathcal{H}_{\mathrm{so}}|{}^5P_2\rangle=0.995(\tfrac{1}{3}\sqrt{\tfrac{7}{2}})\zeta_p+0.1(\tfrac{1}{3}\sqrt{21})\zeta_d.$$

For ζ_p we may substitute 168 cm^{-1} and for ζ_d, 250 cm^{-1}.[14] The coefficient of the quintet state admixed to the septet is then simply this matrix element divided by the energy separation and is given in Eqs. (14).

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Elastic Differential Scattering of He^+ Ions by Ne and Ar and of Ar^+ Ions by Ar in the 10–600-eV Range*

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Absolute elastic differential scattering cross sections of He^+ on Ne and Ar and of Ar^+ on Ar have been measured at relative energies ranging from 10 to 600 eV and scattering angles of 1° to 40°. The He^+ on Ne and Ar cross sections are monotonically decreasing functions of angle and have a superimposed ripple structure which is attributed to curve-crossing effects. No rainbow-angle structure is evident on these curves. The Ar^+-on-Ar cross sections indicate both rainbow scattering and oscillations associated with symmetric charge exchange. From the values of the rainbow scattering angle, the estimated binding energy of Ar_2^+ is 1.6 ± 0.3 eV, assuming the general shape of the attractive potential resembles that of He_2^+.

I. INTRODUCTION

EXPERIMENTAL and theoretical studies of the differential scattering of He^+ on He have shown that there is much to be learned about ion-atom interactions from such studies.[1,2] The $He^+ + He$ elastic interaction was found to be well described by the diabatic ${}^1\Sigma_u{}^+$ and ${}^1\Sigma_g{}^+$ states of He_2^+. A secondary oscillation found at large angles and energies was identified as a manifestation of nuclear symmetry.[3] Another anomaly discovered in the data, a ripple in amplitude of the peaks and valleys, has been attributed to the effect of curve crossing on the elastic scattering.[4]

In this paper we report an experimental study of the differential scattering of He^+ on Ne and Ar, and of Ar^+ on Ar. A theoretical analysis of the scattering cross sections has not been attempted, principally because of the lack of computed interaction potentials for these systems. Since only a single ${}^2\Sigma^+$ state is needed to describe the scattering of He^+ ions by Ne and Ar, these interactions differ from that of $He^+ + He$. The $Ar^+ + Ar$ interaction, however, is more complex and requires perhaps as many as six interaction potentials for its description. This system has recently been studied by Jones *et al.*,[5] who measured the electron capture probability.

Differential cross sections were measured with the apparatus used for the $He^+ + He$ measurements.[1] Attention was focused on elastic scattering studies although some cursory observations of inelastic scattering are also reported. The $He^+ + Ne$ and $He^+ + Ar$ elastic-scattering cross sections are smooth functions of angle with a slight ripple structure which is attributed to curve crossings. The $Ar^+ + Ar$ elastic scattering is rich in structure because of several different interference processes.

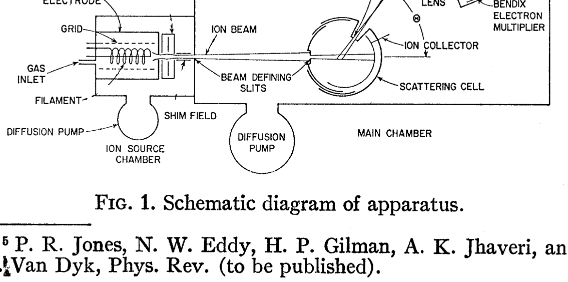

FIG. 1. Schematic diagram of apparatus.

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