

given by

$$\frac{\alpha_1}{\alpha_2} = \left( \frac{R_1^4 n_2}{R_2^4 n_1} \right) \left( \frac{\bar{E}_2^2(1)/\bar{E}_1^2(1)}{\bar{E}_2^2(2)/\bar{E}_1^2(2)} \right). \quad (C3)$$

It is evident that if the ratio

$$\frac{\bar{E}_2^2(1)/\bar{E}_1^2(1)}{\bar{E}_2^2(2)/\bar{E}_1^2(2)} \approx 1, \quad (C4)$$

then

$$\frac{\alpha_1}{\alpha_2} \approx \frac{R_1^4 n_2}{R_2^4 n_1}. \quad (C5)$$

One may conclude from (C5) that it is possible to obtain a rough comparison of the relative magnitudes of the polarizabilities of the constituents of a crystal if one has available an estimate of their relative extensions from, for example, a Fourier projection obtained from x-ray data. This technique has applicability even in crystals which are primarily molecular or covalent in nature which, though well represented by the product approximation, have crystalline potentials which are too complicated in nature to make possible an estimate of the  $\bar{E}$ 's.

## Quadrupole Antishielding Factors of Ions\*

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Values of the quadrupole antishielding factor  $\gamma_\infty$  have been calculated for the  $Mn^{2+}$ ,  $Fe^{3+}$ ,  $Ga^{3+}$ , and  $Ag^+$  ions, using the method of direct solution of the inhomogeneous Schrödinger equation for the perturbed wave functions. For the  $Fe^{3+}$  ion, the present value of  $\gamma_\infty$  ( $= -9.14$ ) is appreciably larger in magnitude than that previously obtained by Burns and Wikner, resulting in a decrease of the calculated quadrupole moment of  $Fe^{57m}$  as deduced from measurements using ferric compounds. The resulting value of  $Q(Fe^{57m})$  is  $+0.28 \times 10^{-24} \text{ cm}^2$ .

### I. INTRODUCTION

VALUES of the quadrupole antishielding factor<sup>1-3</sup> have been recently calculated for the following ions:  $Mn^{2+}$ ,  $Fe^{3+}$ ,  $Ga^{3+}$ , and  $Ag^+$ , using the method of direct solution of the inhomogeneous Schrödinger equation for the perturbed wave functions which has been previously employed by the author.<sup>1-3</sup> The unperturbed wave functions used in this work were the Hartree-Fock functions for the four ions considered.<sup>4-6</sup>

As has been discussed previously,<sup>1-3</sup> the contribution  $\gamma_\infty(nl \rightarrow l)$  due to the radial modes of excitation of the  $nl$  shell is given by

$$\gamma_\infty(nl \rightarrow l) = C_{ll}^{(2)} \int_0^\infty u_0' u_1' r^2 dr, \quad (1)$$

where  $u_0'$  is  $r$  times the radial unperturbed wave func-

tion,  $u_1'$  is  $r$  times the radial part of the perturbation of the wave function due to the field of the nuclear quadrupole moment  $Q$ ;  $u_1'$  is determined by the equation:

$$\left[ -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_0 - E_0 \right] u_1'(nl \rightarrow l) = u_0' \left( \frac{1}{r^3} - \left\langle \frac{1}{r^3} \right\rangle_{nl} \right), \quad (2)$$

and by the orthogonality condition:

$$\int_0^\infty u_0' u_1' dr = 0. \quad (3)$$

In Eq. (1),  $C_{ll}^{(2)}$  represents the factor which arises from the integration over the angular variables and the summation over the magnetic substates. For a completed  $p$  shell, we have  $C_{11}^{(2)} = 48/25$ , whereas for a completed  $d$  shell,  $C_{22}^{(2)} = 16/7$ . For the cases of  $Mn^{2+}$  and  $Fe^{3+}$ , where the  $3d$  shell is half-filled, we have  $C_{22}^{(2)} = 8/7$ . The function  $u_0'$  is normalized to 1:

$$\int_0^\infty u_0'^2 dr = 1. \quad (4)$$

In Eq. (2),  $V_0$  and  $E_0$  are the unperturbed effective potential and energy eigenvalue, respectively, pertain-

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<sup>1</sup> R. M. Sternheimer, Phys. Rev. **84**, 244 (1951).

<sup>2</sup> H. M. Foley, R. M. Sternheimer, and D. Tycko, Phys. Rev. **93**, 734 (1954).

<sup>3</sup> R. M. Sternheimer and H. M. Foley, Phys. Rev. **102**, 731 (1956).

<sup>4</sup> R. E. Watson, Phys. Rev. **118**, 1036 (1960); and Technical Report No. 12, Solid State and Molecular Theory Group, Massachusetts Institute of Technology, 1959 (unpublished) (wave functions for  $Mn^{2+}$  and  $Fe^{3+}$ ).

<sup>5</sup> W. W. Piper, Phys. Rev. **123**, 1281 (1961) (for  $Ga^{3+}$ ).

<sup>6</sup> B. H. Worsley, Proc. Roy. Soc. (London) **A247**, 390 (1958) (for  $Ag^+$ ).

TABLE I. Values of  $\gamma_\infty(nl \rightarrow l)$  for several ions.

Ion	Na <sup>+</sup>	K <sup>+</sup>	Mn <sup>2+</sup>	Fe <sup>3+</sup>	Ga <sup>3+</sup>	Ag <sup>+</sup>
$\gamma_\infty(2p \rightarrow p)$	-5.16	-1.22	-0.75	-0.70	-0.58	-0.32
$\gamma_\infty(3p \rightarrow p)$		-17.15	-9.15	-7.89	-6.42	-2.32
$\gamma_\infty(3d \rightarrow d)$			-2.55	-1.59	-3.29	-0.60
$\gamma_\infty(4p \rightarrow p)$						-20.39
$\gamma_\infty(4d \rightarrow d)$						-13.14
$\gamma_\infty(\text{ang})$	+0.60	+1.05	+1.08	+1.04	+0.79	+1.9
$\gamma_\infty$	-4.56	-17.32	-11.37	-9.14	-9.50	-34.87

ing to the electron shell considered;  $\langle 1/r^3 \rangle_{nl}$  is the average of  $1/r^3$  over the unperturbed wave function  $u_0'$ .

As has been discussed previously,<sup>2,7</sup> the effective values of  $(V_0 - E_0)$  which pertain to a given unperturbed wave function  $u_0'$  are obtained as follows:

$$V_0 - E_0 = \frac{1}{u_0'} \frac{d^2 u_0'}{dr^2} \frac{l(l+1)}{r^2}. \quad (5)$$

The solution  $u_1'(nl \rightarrow l)$  was obtained in the same manner as in our previous work.<sup>1-3</sup> Thus, Eq. (2) was integrated inward starting from a large radius  $r_1$  ( $\sim 4a_H$ ) and was also integrated outward from  $r=0$ , using a power series expansion for  $u_1'$  near the nucleus. The two solutions are joined at an intermediate radius  $r_2$  ( $\sim 0.1-0.2a_H$ ). For the cases of Mn<sup>2+</sup> and Fe<sup>3+</sup>, the inward integrations were performed by means of an IBM 7090 computer. In the actual work, as a check on the calculations, several inward integrations are performed, with different starting values  $u_1'(r_1)$  at  $r_1$ . If the value of  $[l(l+1)/r^2] + V_0 - E_0$  at  $r_1$  is denoted by  $M(r_1)$ , and if  $I(r_1)$  denotes the inhomogeneous term on the right-hand side of Eq. (2) [as evaluated at  $r_1$ ], then the value of  $u_1'(r_1 + \delta_1)$  which is used to start the integration ( $\delta_1$  = interval of integration at  $r_1$ ) is given by

$$u_1'(r_1 + \delta_1) = u_1'(r_1) \exp(-N^{1/2}\delta_1), \quad (6)$$

where  $N$  is defined by

$$N \equiv M(r_1) - [I(r_1)/u_1'(r_1)]. \quad (7)$$

## II. RESULTS AND DISCUSSION

The resulting values of  $\gamma_\infty(nl \rightarrow l)$  as obtained from Eq. (1) are given in Table I. We note that the integrations were carried out for the following states:  $3p$  and  $3d$  for Mn<sup>2+</sup>, Fe<sup>3+</sup>, and Ga<sup>3+</sup>;  $4p$  and  $4d$  for Ag<sup>+</sup>. [The function  $u_1'(4d \rightarrow d)$  for Ag<sup>+</sup> has been obtained previously,<sup>8</sup> and the value of  $\gamma_\infty(4d \rightarrow d) = -13.14$  has already been given in Table III of reference 8.]<sup>9</sup> For

<sup>7</sup> R. M. Sternheimer, Phys. Rev. **96**, 951 (1954); **107**, 1565 (1957); **115**, 1198 (1959).

<sup>8</sup> R. M. Sternheimer, Phys. Rev. **127**, 812 (1962).

<sup>9</sup> Tables of the perturbed wave functions  $u_1'(nl \rightarrow l)$  obtained in the present work are given in a supplementary paper "Wave Functions for Quadrupole Antishielding Factors." This supplementary paper has been deposited as Document No. 7475 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting \$2.50

all of the ions, the value of  $\gamma_\infty(2p \rightarrow p)$  was obtained by interpolation of the previously calculated results<sup>3</sup> for  $\gamma_\infty(2p \rightarrow p)$  of Cl<sup>-</sup>, Cu<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>. Since  $\gamma_\infty(2p \rightarrow p)$  makes a relatively small contribution to the total  $\gamma_\infty$  ( $\lesssim 8\%$ ), the uncertainty in the interpolation procedure [ $\pm 0.05$  in  $\gamma_\infty(2p \rightarrow p)$ ] leads to a completely negligible error in the antishielding factor  $\gamma_\infty$ . For Ag<sup>+</sup>, the values of  $\gamma_\infty(3p \rightarrow p)$  and  $\gamma_\infty(3d \rightarrow d)$  were obtained by interpolation of the previously calculated results for Cu<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> (see Table I of reference 3). As in the case of  $\gamma_\infty(2p \rightarrow p)$ , the uncertainty introduced by the interpolation procedure used for  $\gamma_\infty(3p \rightarrow p)$  and  $\gamma_\infty(3d \rightarrow d)$  of Ag<sup>+</sup>, namely,  $\lesssim \pm 0.5$ , is quite negligible compared to the total  $\gamma_\infty$  for the Ag<sup>+</sup> ion (-34.9). The values of the term  $\gamma_\infty(\text{ang})$  in Table I, pertaining to the angular excitations of the four ions, have been obtained from the work of Burns and Wikner,<sup>10</sup> which is based on the Thomas-Fermi expression for  $\gamma_\infty(\text{ang})$  first derived by Sternheimer.<sup>11</sup>

The values of  $\gamma_\infty(np \rightarrow p)$  and  $\gamma_\infty(nd \rightarrow d)$  which have been calculated in the present work can be compared with those obtained by Burns and Wikner<sup>10</sup> using a variational method.<sup>12</sup> For  $\gamma_\infty(nd \rightarrow d)$ , the agreement is reasonably good (to  $\lesssim 15\%$ ). However, for  $\gamma_\infty(np \rightarrow p)$  of the outermost  $p$  shell, the variational values are considerably too small in all cases. Thus for Fe<sup>3+</sup>, Ga<sup>3+</sup>, and Ag<sup>+</sup>, the ratio  $\rho(np)$  of the variational value to the present value for  $\gamma_\infty(np \rightarrow p)$  pertaining to the outermost  $p$  shell is as follows:  $\rho(3p) = 5.00/7.89 = 0.634$  for Fe<sup>3+</sup>,  $\rho(3p) = 4.08/6.42 = 0.636$  for Ga<sup>3+</sup>, and  $\rho(4p) = 10.91/20.39 = 0.535$  for Ag<sup>+</sup>. A similar result was previously noted by Wikner and Das<sup>13</sup> for Rb<sup>+</sup>  $4p$  and Cs<sup>+</sup>  $5p$ . The corresponding values of  $\rho$  are as follows:  $\rho = 46.87/66.6 = 0.704$  for Rb<sup>+</sup>  $4p$  and  $\rho = 102.4/129.3 = 0.792$  for Cs<sup>+</sup>  $5p$ . We note that the values of  $\gamma_\infty(nl \rightarrow l)$  calculated according to the present method (solution of the inhomogeneous Schrödinger equation) are believed to be accurate to within 3%. The disagreement of the variational results with the

TABLE II. Values of  $J(nl \rightarrow l)$  and  $\langle r^{-3} \rangle_{nl}$  for the Mn<sup>2+</sup>, Fe<sup>3+</sup>, Ga<sup>3+</sup>, and Ag<sup>+</sup> ions. ( $\langle r^{-3} \rangle_{nl}$  is in units  $a_H^{-3}$ .) All values of  $J(nl \rightarrow l)$  are positive.

Perturbation	$J(nl \rightarrow l)$	$\langle r^{-3} \rangle_{nl}$
Mn <sup>2+</sup> $3p \rightarrow p$	822.1	46.58
Mn <sup>2+</sup> $3d \rightarrow d$	9.325	4.250
Fe <sup>3+</sup> $3p \rightarrow p$	1034	56.17
Fe <sup>3+</sup> $3d \rightarrow d$	12.18	5.724
Ga <sup>3+</sup> $3p \rightarrow p$	2433	108.1
Ga <sup>3+</sup> $3d \rightarrow d$	34.18	11.83
Ag <sup>+</sup> $4p \rightarrow p$	4009	88.53
Ag <sup>+</sup> $4d \rightarrow d$	39.48	8.11

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<sup>10</sup> G. Burns and E. G. Wikner, Phys. Rev. **121**, 155 (1961).

<sup>11</sup> R. M. Sternheimer, Phys. Rev. **80**, 102 (1950).

<sup>12</sup> T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956).

<sup>13</sup> E. G. Wikner and T. P. Das, Phys. Rev. **109**, 360 (1958).

TABLE III. Summary of the values of  $\gamma_\infty$  obtained by direct solution of Eq. (2). The notation (H) indicates that the unperturbed wave functions were Hartree functions. In all other cases, Hartree-Fock wave functions were used in the calculations.

Ion	$\gamma_\infty$	Reference
H <sup>-</sup>	+1.131	b
He	+0.424	b
Li <sup>+</sup>	+0.263	b
Be <sup>2+</sup>	+0.189	b
B <sup>+</sup>	+0.768	b (H)
Na <sup>+</sup>	-4.56	b
Cl <sup>-</sup>	-56.6	a
K <sup>+</sup>	-17.32	b
Mn <sup>2+</sup>	-11.37	c
Fe <sup>3+</sup>	-9.14	c
Cu <sup>+</sup>	-15.0	a
Ga <sup>3+</sup>	-9.50	c
Rb <sup>+</sup>	-70.7	a (H)
Ag <sup>+</sup>	-34.87	c
Cs <sup>+</sup>	-143.5	a (H)

<sup>a</sup> See reference 3.

<sup>b</sup> R. M. Sternheimer, Phys. Rev. 115, 1198 (1959).

<sup>c</sup> Present work.

present values probably arises from two effects: (1) the fact that the perturbed wave function  $u_1'$  is forced to be proportional to  $u_0'$  in the variational method; (2) the orthogonalization procedure<sup>14</sup> employed in references 10 and 13.

In Table I, we have also listed for convenience the results previously obtained<sup>7</sup> for Na<sup>+</sup> and K<sup>+</sup>. Thus Table I of the present paper together with Table I of reference 3 give a complete listing of the values of  $\gamma_\infty(nl \rightarrow l)$  which contribute to the calculated antishielding factors  $\gamma_\infty$ . We note that unlike the other 4 cases, the values of  $\gamma_\infty(\text{ang})$  for Na<sup>+</sup> and K<sup>+</sup> have been obtained<sup>7</sup> from a complete solution of the equations for the perturbed wave functions  $u_1'$  pertaining to the various angular modes of excitation:  $ns \rightarrow d$  and  $np \rightarrow f$ .

In connection with  $\gamma_\infty$  for Fe<sup>3+</sup>, we note that our value, namely,  $\gamma_\infty = -9.14$ , is considerably larger in magnitude than that obtained by Burns and Wikner<sup>10</sup> (-6.17). As a result, the value of the quadrupole

moment of Fe<sup>57m</sup>, which has been calculated by Burns<sup>15</sup> to be  $\cong +0.4 \times 10^{-24}$  cm<sup>2</sup> from measurements on ferric compounds, will be reduced to the following value when our result for  $\gamma_\infty$  is used:

$$Q(\text{Fe}^{57m}) \cong +0.4 \times (7.17/10.14) \times 10^{-24} \\ = +0.28 \times 10^{-24} \text{ cm}^2. \quad (8)$$

Here (7.17/10.14) is the ratio of the values of  $(1 - \gamma_\infty)$  from the two calculations. The result of Eq. (8) decreases the discrepancy between the values of  $Q(\text{Fe}^{57m})$  obtained from ferric salts and those derived from ferrous compounds ( $\sim 0.15 \times 10^{-24}$  cm<sup>2</sup>), which has been recently discussed by Ingalls.<sup>16</sup>

Table II gives the values of  $\langle r^{-3} \rangle_{nl}$  obtained from the zero-order wave functions,<sup>4-6</sup> and the values of the integrals  $J(nl \rightarrow l)$ :

$$J(nl \rightarrow l) \equiv \int_0^\infty u_0' u_1' (nl \rightarrow l) r^{-3} dr. \quad (9)$$

As discussed in reference 8,  $J(nl \rightarrow l)$  enters into the calculation of the second-order quadrupole effect for the hyperfine structure (energy  $\propto Q^2$ ).

In Table III, we have given a summary of the values of the antishielding factor  $\gamma_\infty$  which we have obtained in the present work and in two previous papers.<sup>3,7</sup> In all of the cases  $u_1'$  was obtained by direct solution of Eq. (2), and the resulting values of the total  $\gamma_\infty$  are estimated to be accurate to  $\sim 5\%$  for the given unperturbed wave functions used in the calculations. As indicated in the table, in all but three cases, Hartree-Fock wave functions (including exchange) were used in obtaining  $\gamma_\infty$ .

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<sup>14</sup> P. G. Khubchandani, R. R. Sharma, and T. P. Das, Phys. Rev. 126, 594 (1962).

<sup>15</sup> G. Burns, Phys. Rev. 124, 524 (1961).

<sup>16</sup> R. Ingalls, Phys. Rev. 128, 1155 (1962).