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Effect of Stress on the Trigonal Splittings of d^3 Ions in Sapphire (α-Al_2O_3)†

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We have measured the effect of uniaxial stress on the trigonal splittings of the ground ($^4A_2$) state and the first excited (^2E) state of the $(3d)^3$ ions V^{2+}, Cr^{3+}, and Mn^{4+} in Al_2O_3. We find that compression along the c axis alters the ground-state splitting $2D$ by an amount which is almost independent of the ionic charge. The effect on the excited-state splitting Λ, on the other hand, varies markedly through the isoelectronic sequence, changing sign on going from Cr^{3+} to Mn^{4+}. Previous work by Macfarlane has shown that Λ depends primarily on the diagonal trigonal field parameter v, while $2D$ depends primarily on the off-diagonal parameter v'. We tentatively suggest that our data show that in Al_2O_3, v' depends predominantly on long-range interactions, while v depends more on the immediate environment of the chromophoric ion. Data are also given concerning the effect on the ^2E splitting of stress perpendicular to the c axis, and concerning the shift of the ^2E level as a whole under stress.

INTRODUCTION

IONS of the $(3d)^3$ isoelectronic sequence show well-resolved spin resonance and optical spectra when dissolved substitutionally in oxide lattices. In α-Al_2O_3, these spectra show level splittings which arise from the trigonal symmetry of the host lattice. A great deal has been written about the trigonal splittings in ruby (Al_2O_3:Cr^{3+}).[1–7] In particular, the splitting of the $^4A_2$ ground state has aroused a lot of interest, since it appeared from early work[1] that conventional crystal-field theory could not account either for its sign or its magnitude. However, recent work by Macfarlane[7] has shown that if the crystal-field calculations are carried through correctly they can account quite accurately for the ground-state splitting, as well as for the splitting of the excited states. Subsequently, Sturge,[8] using Hemphill and Donoho's[9] data on the ground state, showed that Macfarlane's theory would also account for the variation of the splittings under uniaxial stress (applied parallel to the c axis, so as to change the trigonal field but not to reduce the symmetry).[10] Macfarlane[11] has recently shown that his theory will also account for the stress-induced splittings in cubic crystals, and has given algebraic formulas for the splittings of the ground and lowest excited states.[12]

Macfarlane[7,12] finds that the principal contribution to the splitting of the lowest excited state (^2E, the state from which the well-known R-line fluorescence originates) is proportional to the on-diagonal trigonal field parameter v.[13] The principal contribution to the ground ($^4A_2$) state splitting (which can be found by spin resonance) is proportional to the off-diagonal trigonal field parameter v'.[13] Thus, small changes in these splittings induced by stress can be interpreted as changes in the corresponding trigonal field parameters. Furthermore, by following the effects of stress through an isoelectronic sequence of ions, we have in principle a

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[9] R. B. Hemphill, P. L. Donoho, and E. D. MacDonald, Phys. Rev. **146**, 329 (1966).

[10] Agreement between theory and experiment in Ref. 8 is not quite as good as was therein indicated. The data of Ref. 9 [at that time unpublished but quoted by P. L. Donoho, Phys. Rev. **133**, A1080 (1964)] were misinterpreted to obtain an "experimental" value for the change in ground-state splitting $2\Delta D$ which was $\frac{2}{3}$ of the true value. Thus, the results of Ref. 8 show that Macfarlane's theory accounts for about 60% of the stress effect, rather than nearly 100% as claimed. (We get the same result if we calculate ΔD directly from the data of Ref. 8 using the formulas of Ref. 12.) The discrepancy is in the direction to be expected if there is a weak Ham effect in the $^2T_1$ and $^2T_2$ states, which will reduce the apparent value of $\Delta v'$ [F. S. Ham, Phys. Rev. **138**, A1727 (1965); W. C. Scott and M. D. Sturge, *ibid.* **146**, 262 (1966)].

[11] R. M. Macfarlane, Phys. Rev. **158**, 252 (1967).

[12] R. M. Macfarlane, J. Chem. Phys. **47**, 2066 (1967).

[13] These one-electron trigonal field parameters are defined by M. H. L. Pryce and W. A. Runciman [Discussions Faraday Soc. **26**, 34 (1958)] as $v = -3\langle t_2\pm \mid V_{\text{trig}} \mid t_2\pm\rangle$, $v' = \langle t_2\pm \mid V_{\text{trig}} \mid e\pm\rangle$. (See the original reference for definitions of the basis functions $\mid t_2\pm\rangle$ and $\mid e\pm\rangle$.)

method of separating those effects which depend critically on the ion from those which depend primarily on the host lattice.

We are fortunate in having available three ions of the $(3d)^3$ isoelectronic sequence, V^{2+}, Cr^{3+}, Mn^{4+}, all of which enter the Al_2O_3 lattice substitutionally and occupy sites of trigonal symmetry.[1,14,15] V^{2+} ions are produced by γ irradiation of $Al_2O_3:V^{3+}$. The charge-compensating defects are presumably distributed at random throughout the crystal. Since the microwave and optical spectra show that the V^{2+} ion is at a site of accurately trigonal symmetry,[14,16] charge compensation cannot be local. The Mn^{4+} ions are also at trigonal sites.[15,16] However, in this case charge compensation is achieved by adding Mg^{2+} during crystal growth. It is possible that the Mg^{2+} ions, instead of being distributed throughout the crystal, occupy the Al^{3+} site nearest to the Mn^{4+} ion. Since this site lies on the trigonal axis through the impurity site, the symmetry would still be trigonal and this type of local charge compensation cannot be excluded by the data.

In this paper we report the effect of stress on the $^4A_2$ and ^2E splittings of these three ions (most of the data on Cr^{3+} have been previously reported by other authors).[8,9,17] We are able to tentatively conclude from our data that v depends primarily on the ion and its immediate surroundings, while v' is determined primarily by the lattice and is not very dependent on the ion involved.

SPIN-RESONANCE MEASUREMENTS

The splitting of the $^4A_2$ ground level is denoted $2D$, which is the amount the $m_s=\pm\frac{3}{2}$ states are raised above the $m_s=\pm\frac{1}{2}$ states by the combined action of trigonal field and spin-orbit coupling. We measured the change in D produced by uniaxial compression, working at X band (9000 Mc/sec) with equipment described elsewhere.[18] Pressure was applied along the c axis (trigonal axis) of the crystal, with the magnetic field perpendicular to it. (This geometry was dictated by the nature of the experimental setup.) The cavity frequency ν changes in a known way with the pressure P, and we can relate the observed shift in field for resonance $(dH/dp)_{\text{obs}}$ to the change in zero-field splitting through the expression

$$\begin{aligned}(dH/dp)_{\text{obs}}-(\partial H/\partial\nu)_D(d\nu/dp)&=(\partial H/\partial p)_\nu\\&=\Delta H_{\text{corrected}}\\&=(\partial H/\partial D)_\nu\Delta D.\qquad(1)\end{aligned}$$

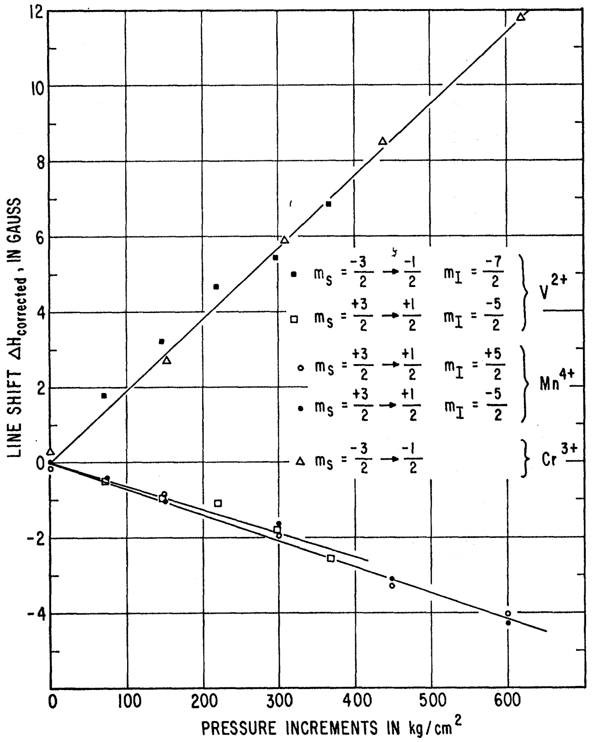

FIG. 1. Effect of compressive stress parallel to the c axis on the positions of the $m_s=\pm\frac{3}{2}\to\pm\frac{1}{2}$ transitions of V^{2+}, Cr^{3+}, and Mn^{4+} in Al_2O_3. The corresponding changes in the ground-state splittings are obtained by multiplying these shifts by appropriate coefficients, as explained in the text.

Here $\Delta D=dD/dp$, and $\Delta H_{\text{corrected}}$ denotes the shift in resonant field, corrected for the change in frequency. The coefficients $(\partial H/\partial D)_D$ and $(\partial H/\partial D)_\nu$ are evaluated, for the zero-stress values of ν and D, from the slopes of the relevant curves obtained from a computer program that diagonalizes the spin Hamiltonian.

For V^{2+}, one hyperfine line was monitored for each of the electronic transitions $m_s=\pm\frac{3}{2}\to\pm\frac{1}{2}$. For Mn^{4+}, two hyperfine lines from the low-field $m_s=+\frac{3}{2}\to+\frac{1}{2}$ transition were monitored since the $m_s=-\frac{1}{2}\to-\frac{3}{2}$ lines were so broad that they could not be resolved. The experimental results are shown in Fig. 1, with our results for Cr^{3+} (which agree with those of Ref. 9) included for the sake of completeness. The measurements on V^{2+} and Cr^{3+} were made at 77°K; those on Mn^{4+} were made at 1.4°K, to improve the signal-to-noise ratio.

Our measurements yield, for unit compressive stress, $\Delta D=-20.3\times10^{-13}$ cm/dyn for V^{2+}, -20.3×10^{-13} cm/dyn for Cr^{3+}, and -31.8×10^{-13} cm/dyn for Mn^{4+}; the error is $\pm10\%$ in each case. It can be seen from the figure that the actual measured shift of the lines is (coincidentally) essentially the same for all ions; the differences in induced D terms result from the different values of the coefficient $(\partial H/\partial D)_\nu$ for the different ions. The relative increments in D for an applied pressure of

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[14] M. D. Sturge, Phys. Rev. **130**, 639 (1963).

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[16] N. Laurence and J. Lambe, Phys. Rev. **132**, 1029 (1963).

[17] A. L. Schawlow, *Advances in Quantum Electronics*, edited by J. R. Singer (Columbia University Press, New York, 1961), Vol. 2, p. 50; A. A. Kaplyanskii and A. K. Przhevuskii, Dokl. Akad. Nauk SSSR **142**, 313 (1962) [English transl.: Soviet Phys.—Doklady **7**, 37 (1962)].

[18] Elsa Feher, Phys. Rev. **136**, A145 (1964).

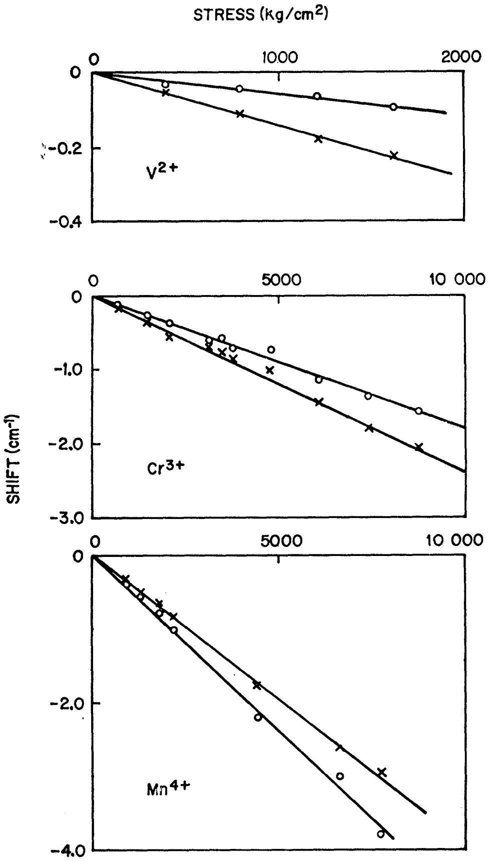

FIG. 2. Displacements of the R lines (from their zero-stress positions) under compressive stress parallel to the c axis, in Al_2O_3 doped with V^{2+}, Cr^{3+}, and Mn^{4+}. (Note the changes in scale.) The change in ground-state splitting is too small to show up on this scale, and all the stress effects shown come from the excited states. ○: $R_1(\bar{E}\rightarrow{}^4A_2)$; ×: $R_2(2\bar{A}\rightarrow{}^4A_2)$.

1 dyn/cm² are $\Delta D/D=12.8\pm1.3\times10^{-12}$ for V^{2+}, $10.6\pm1.1\times10^{-12}$ for Cr^{3+}, and $16.4\pm1.6\times10^{-12}$ for Mn^{4+}.

OPTICAL MEASUREMENTS

All three ions show strong sharp line fluorescence from the ^2E level to the ground state.[1,14,15] In Al_2O_3, the ^2E level is split by the trigonal crystal field into $2\bar{A}$ and $\bar{E}$ states, of which the former is highest.[19] The splitting Λ is defined as $E(2\bar{A})-E(\bar{E})$. At 77°K, the temperature of all the measurements, sharp line fluorescence is observed from both states. In V^{2+} and Cr^{3+} the ground-state splitting is resolved, but its change under stress is too small to detect optically (roughly 0.03 cm^{-1} at 10^{10} dyn/cm² from the data in the previous section). Stress was applied to the crystals (oriented by x rays to within 2°) as described previously.[20] To obtain stresses above 20 kg/mm² in a typical sample of 5-mm² cross section, it was necessary to replace the weights of Ref. 20 by a pneumatic press. The unpolarized spectra were recorded photoelectrically by a Jarrell-Ash 1.8-m spectrometer, with a resolution of 0.05 cm^{-1}.

The results for uniaxial stress applied parallel and perpendicular to the c axis are shown in Figs. 2 and 3. The points represent the shift of the centroids of the lines from their positions in zero stress. For the sharp lines of V^{2+} and Cr^{3+}, the centroids and line maxima agree, but in Mn^{4+}, which has lines 2 to 3 cm^{-1} wide, the positions of the centroids could be found considerably more precisely than the maxima.

We made a least-squares fit to the data of Figs. 2 and 3 and obtained the linear terms in the shift ΔE_m of the

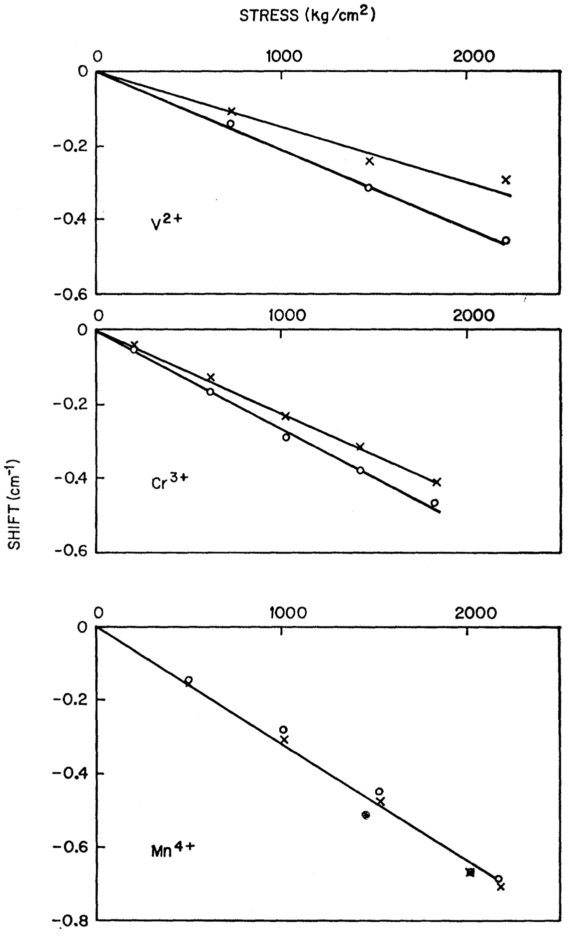

FIG. 3. Same as Fig. 2, for stress perpendicular to the c axis (along $\langle 11\bar{2}0\rangle$): ○: R_1; ×: R_2.

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[19] The sign of the splitting in V^{2+} and Cr^{3+} is known from the relative intensities of the emission lines in σ and π polarization, which are in good agreement with the theory of Ref. 1. In Mn^{4+} the relative intensities are not in agreement with this theory, and the sign was not determined in Ref. 15. Recently M. H. Crozier [Phys. Letters **18**, 219 (1965)] has observed the Zeeman effect in Al_2O_3:Mn^{4+} at 77°K and 100 kG. His Zeeman patterns are consistent with C_3 selection rules only if the sign of the splitting is the same (positive Λ) as in V^{2+} and Cr^{3+} [M. H. Crozier (private communication)]. A careful check of the Zeeman spectrum at 4°K and 70 kG by K. A. Ingersoll (unpublished) confirms this.

[20] A. L. Schawlow, A. H. Piksis, and S. Sugano, Phys. Rev. **122**, 1469 (1961).

mean position E_m of the lines, and the change in their splitting. These are given in Table I. (We define $\Delta E_m \equiv dE_m/dp$, $\Delta\Lambda \equiv d\Lambda/dp$, where p is the stress in dyn/cm^2.) The data on Cr^{3+} are in agreement with previous work.[17]

We could find no evidence for quadratic or higher terms in the shift or splitting. We looked especially carefully for such terms in ruby. The quadratic term in ΔE_m was found to be less than 10^{-21} cm^3/dyn^2. A quadratic term of this order (roughly 10^4 cm^{-1} at unit strain) is required to account for the effect of temperature on the widths and positions of the R lines.[21]

DISCUSSION

We may quickly dispose of those data given in the previous section which are not relevant to the question of how trigonal fields vary under stress. The shift in the mean energy E_m is primarily due to the hydrostatic component of stress (although there is a substantial second-order effect of trigonal field,[7] which accounts for the different mean shifts induced by stress parallel and perpendicular to the c axis). Hydrostatic pressure has the general effect of increasing covalency; as expected, the effect increases as we go to the more highly charged, more strongly covalent ion. As in the cases of V^{2+} and Cr^{3+} in MgO,[20,22] the shift to lower frequencies shows that the covalent reduction in the interelectronic repulsion (represented by the Racah parameters B and C) dominates over the increase in the cubic crystal-field parameter $10Dq$.

The effect on the ^2E splitting of compressive stress perpendicular to the c axis is qualitatively the same as that of a somewhat smaller tensile stress parallel to it and (within experimental error) independent of direction in the basal plane. This is to be expected from our ordinary ideas about elasticity; quantitative interpretation would require more information about how the ions close to the impurity move when stress is applied.

TABLE I. Summary of the experimental data on the effect of stress on the R lines of $(3d)^3$ ions in Al_2O_3.

Ion	Stress direction	$\Delta\Lambda$[a] 10^{-11} cm/dyn	ΔE_m[b]
V^{2+}	$\langle 0001 \rangle$	-9.0 ± 0.7	-10 ± 1
	$\langle 11\bar{2}0 \rangle$	$+7.5\pm1.5$	-18 ± 2
Cr^{3+}	$\langle 0001 \rangle$	-5.8 ± 0.3	-21.5 ± 1
	$\langle 11\bar{2}0 \rangle$	$+3.8\pm0.4$	-28 ± 1
	$\langle 10\bar{1}0 \rangle$	3.5 ± 0.4	-26 ± 2
Mn^{4+}	$\langle 0001 \rangle$	$+7\pm2$	-42 ± 3
	$\langle 11\bar{2}0 \rangle$	-1 ± 2	-33 ± 3

[a] $\Delta\Lambda = d\Lambda/dp$, where $\Lambda = E(2\bar{A}) - E(\bar{E})$. Negative $\Delta\Lambda$ means that Λ decreases under compression.

[b] $\Delta E_m = dE_m/dp$, where $E_m = \frac{1}{2}[E(2\bar{A}) + E(\bar{E})] - E(^4A_2)$.

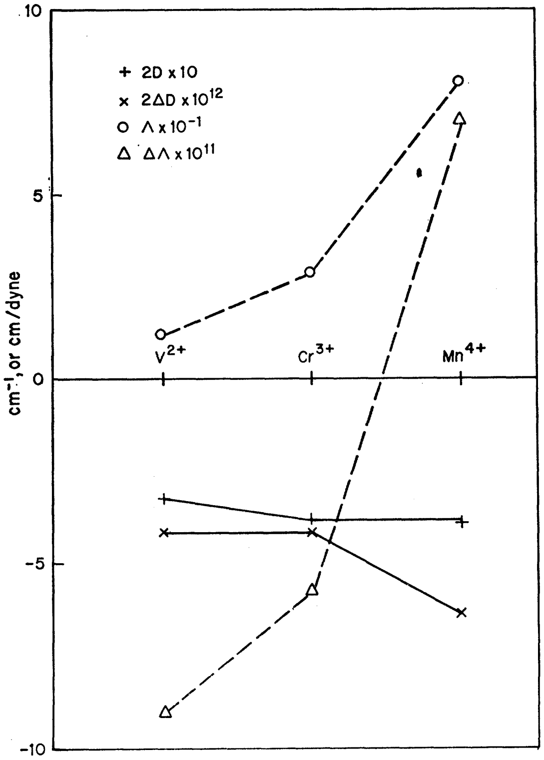

FIG. 4. Trigonal splittings of the ^2E and $^4A_2$ levels, and the effect of compressive stress on them, as a function of ionic charge.

The changes in the ground-state and excited-state splittings under uniaxial stress parallel to the c axis are shown as a function of ionic charge in Fig. 4, along with the absolute values of the splittings.[1,14,15,19] Qualitatively, we note that the effect of stress on the ground-state splitting, like the splitting itself, varies only slightly from ion to ion. On the other hand, the effect on the excited-state splitting varies even more markedly than the excited-state splitting itself, changing sign as we go from Cr^{3+} to Mn^{4+}.[23]

Quantitatively, we can interpret the data in terms of Macfarlane's theory.[7,12] He accounts[7] very successfully for the observed trigonal splittings of V^{2+} and Cr^{3+} in Al_2O_3 with two semiempirical trigonal field parameters v and v'.[13] He obtains[12] approximate lowest-order perturbation expressions that are accurate enough for our purposes (15% in the case of ruby). The leading terms in these expressions are

$$\Lambda = 4\zeta v/3D_7,$$

$$2D = -2\sqrt{2}\zeta^2 v'(2/3D_1D_4 + 1/D_2D_3 + 1/D_2D_4). \quad (2)$$

Here ζ is the one-electron spin-orbit coupling param-

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[21] D. E. McCumber and M. D. Sturge, J. Appl. Phys. **34**, 1682 (1963).

[22] M. D. Sturge, Phys. Rev. **131**, 1456 (1963).

[23] Microwave-optical measurements by G. F. Imbusch, S. R. Chinn and S. Geschwind [Phys. Rev. **161**, 295 (1967)] [see also M. H. Crozier, Phys. Letters **18**, 219 (1965)] have confirmed that the sharp line emission of Mn^{4+} in Al_2O_3 comes from the same trigonal site that is seen in spin resonance.

TABLE II. Cubic field parameters in cm^{-1} and calculated trigonal field effects for $(3d)^3$ ions in Al_2O_3.

	V^{2+}	Cr^{3+}	Mn^{4+}
$10Dq$	15 000	18 000	21 000
B	550	650	700
C	2 475	3 120	3 150
ζ	120	170	200
Λ/v	0.029	0.035	0.038
$2D/v'$	-2.85×10^{-4}	-4.5×10^{-4}	-6.8×10^{-4}

eter, and the D's are energy differences between cubic terms which are defined in Ref. 12. They can be calculated from the matrices of Tanabe and Sugano,[24] with the parameters given in the first three rows of Table II. With the assumed values of ζ, we obtain the ratios Λ/v, $2D/v'$, given in the last two rows. These are probably accurate to about 20%.

In Table III we give the values of v, v', Δv, and $\Delta v'$ which we derived from the experimental splittings using the ratios given in Table II. McClure[25] has calculated v and v' from the point-charge model. His formulas can be written

$$v=b_2\langle r^2\rangle+b_4\langle r^4\rangle,$$

$$v'=-\tfrac{1}{3}\sqrt{2}b_2\langle r^2\rangle+\tfrac{1}{4}\sqrt{2}b_4\langle r^4\rangle. \tag{3}$$

For an undistorted Al_2O_3 lattice with an impurity ion exactly at the Al^{3+} site, McClure finds $b_2=-540$ cm^{-1}, $b_4=+20$ cm^{-1}, with r in atomic units. Using Watson's[26] self-consistent-field (SCF) wave functions to give us $\langle r^2\rangle$ and $\langle r^4\rangle$,[14] we obtain the "model" values of v and v' given in Table III. The absolute values of v and v' depend on the details of the model (in particular on the ionic positions), and no great significance can be attached to them. The trend from ion to ion, on the other hand, is determined almost entirely by the variation of $\langle r^2\rangle$ and is a significant test of the model. We note that v' and $\Delta v'$ follow the expected trend quite well, while v and Δv go in the opposite sense.

The agreement with the point-charge calculation suggests strongly that the major contribution to v' is the relatively long-range (quadrupolar) electrostatic interaction between rigid ions [this is the first and dominant term in Eq. (3)]. It is in principle possible that induced dipolar interactions[27] are also important. These contribute to the $\langle r^2\rangle$ terms in Eq. (3), and in a fixed lattice would show the same trend as the rigid-ion term, decreasing with decreasing ionic radius. It seems fairly certain that covalent effects, which increase rapidly with ionic charge, are not very important to v'.

The opposite appears to be the case for v. However, before jumping to the conclusion that covalency is primarily responsible for the anomalous behavior of v, let us look at the data for MgO stressed along a $\langle 111\rangle$ direction. The stress splitting of the $^4A_2$ and ^2E levels of V^{2+} [22,28] and of Cr^{3+} [20,29] (occupying cubic sites in MgO) have been reported. It has been shown[11,20,22] that the values of Δv and $\Delta v'$ for both ions are in quite good agreement with the predictions of the point-charge model. Since the degree of covalency should be much the same in the two host crystals, it appears that we cannot account for the anomalous values of v in Al_2O_3 by invoking covalency.

One important difference between MgO and Al_2O_3 is that in the former all ions are at centers of symmetry. For this reason there can be no induced dipolar effects in MgO.[30] However, as remarked earlier, induced dipolar effects should decrease with decreasing ionic radius, while in Al_2O_3 v increases.

The O_h symmetry in MgO requires that the ions only move in a specified way when perturbed, either by the presence of an impurity ion or by external stress. In Al_2O_3, the C_3 site symmetry permits much greater freedom of movement. Artman and Murphy[31] have taken local ionic displacements into account in a calculation of the trigonal field in $Al_2O_3{:}Cr^{3+}$. This calculation includes both point-charge and induced dipolar contributions. The results are sensitive to the displacements, which are not well known. By choosing a particular set of displacements, Artman and Murphy can account for the observed value of v in Al_2O_3. However, if we calculate v' from their results [using Eq. (3)], we find that it is large and negative.[32] While

TABLE III. Trigonal field parameters for Al_2O_3, calculated from the data, and from the point-charge model (v and v' in cm^{-1}; Δv and $\Delta v'$ in cm^{-1} per 10^9 dyn/cm^2 applied stress).

	V^{2+}	Cr^{3+}	Mn^{4+}
v (from data)	420	830	2100
v (from model)	−1290	−870	−650
v' (from data)	1100	840	570
v' (from model)	590	400	300
Δv	−3.1	−2.3	+1.8
$\Delta v'$	+14.2	+9.0	+9.2

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[24] Y. Tanabe and S. Sugano, J. Phys. Soc. Japan **9**, 766 (1958).

[25] D. S. McClure, J. Chem. Phys. **36**, 2757 (1962).

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

[27] R. R. Sharma and T. P. Das, J. Chem. Phys. **41**, 3581 (1964).

[28] E. Feher, Bull. Am. Phys. Soc. **10**, 699 (1965).

[29] G. D. Watkins and E. Feher, Bull. Am. Phys. Soc. **7**, 29 (1962).

[30] This is not precisely true, since the very presence of an impurity lowers the symmetry at adjacent sites. One might expect the dipoles induced on its neighbors by the impurity to be rather small, compared with those induced in Al_2O_3 by the entire lattice.

[31] J. O. Artman and J. C. Murphy, Phys. Rev. **135**, A1622 (1964).

[32] Artman and Murphy (Ref. 31) contend that v' must be small when the crystal field is strong ($Dq\gg B$) as it is in $Al_2O_3{:}Cr^{3+}$. This is incorrect. The value of v' does not depend on Dq/B, though its importance does. In the limit $Dq/B\rightarrow\infty$, v' can have no effect on the energy levels, but the work of Macfarlane (Refs. 7, 12) shows that this limit is by no means reached in oxides.

one could presumably find a set of displacements which would account for the values of v and v' observed for each ion, the exercise seems hardly worthwhile.

The Mn^{4+} ion may be locally charge compensated by an Mg^{2+} ion in the nearest Al^{3+} site, which lies on the trigonal axis. If this is the case, the data show that v' is insensitive to the presence of the Mg^{2+} ion, reinforcing the argument that v' depends only on a long-range interaction.

To sum up, we have found that in Al_2O_3 the ground-state splitting of a $(3d)^3$ ion and the effect of stress upon it varies only slowly from ion to ion, and varies in the sense predicted by the point-charge model. The ^2E splitting, on the other hand, varies greatly from ion to ion, and the effect of stress varies even more dramatically. Interpreting these results in terms of Macfarlane's theory, we conclude that in Al_2O_3 v' depends primarily on long-range electrostatic interactions, whereas v depends on short-range interactions and may be sensitive to local rearrangements of the ions and possibly to local charge compensation. To our knowledge no microscopic theory[33] has so far been put forward which predicts this pronounced difference between v and v'.

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[33] See, for instance, D. E. Rimmer and D. F. Johnston, Proc. Phys. Soc. (London) **89**, 953 (1966); R. Englman, J. Chem. Phys. **45**, 3862 (1966); and K. Zdansky, Phys. Rev. **159**, 201 (1967).

PHYSICAL REVIEW VOLUME 172, NUMBER 2 10 AUGUST 1968

Mössbauer Measurements with K^{40}†*

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This paper describes an investigation in which the 29.4-keV γ ray formed in the neutron capture reaction $K^{39}(n,\gamma)K^{40}$ was studied by use of the Mössbauer effect. Several potassium compounds were used as the neutron targets, i.e., as γ-ray sources for Mössbauer measurements. The results are: (a) All spectra show a single absorption line at $v=0$ whose width is no more than 1.3 times the minimum predicted from the lifetime; (b) the background and the recoilless fraction vary strongly from one case to another; and (c) the quadrupole splitting and isomer shifts are small if not zero. The recoilless fraction was measured as a function of temperature for a KF target. By fitting the results to curves based on a simple theory of diatomic solids, a value for the effective Debye temperature of potassium in these targets was obtained. In order to arrive at a value of $\delta\langle r^2\rangle/\langle r^2\rangle$ for the K^{40} nucleus, four careful center-shift measurements were carried out with K metal at 10°K and KF at 10, 55, and 80°K as targets, and KCl at 80°K as absorber. Comparison of these results with calculations of the thermal shifts based on our determinations of the effective Debye temperatures of the different targets shows that the measured line shifts are mainly due to thermal shifts. The accuracy of the measurements is sufficient to place an upper limit of $\delta\langle r^2\rangle/\langle r^2\rangle \leq 5\times10^{-4}$ for K^{40}.

I. INTRODUCTION

Of all nuclides with suitable properties for the Mössbauer effect, the one with lowest Z is K^{40}—but it does not have a radioactive parent. Two groups[1,2] have investigated nuclear reactions, one by (n,γ) reactions[1] and the other by (d,p),[2] as a means of forming a suitable number of excited K^{40} nuclei in an appropriate chemical or solid-state environment. The neutron-capture method proved to be the more useful one, and provided quantitative results. In particular, within the large experimental error, the result of Hafemeister and Shera,[1] using the (n,γ) reaction, showed no isomer shift between K and KF. This led to the conclusion that the fractional change of the expectation value of the squared nuclear charge radius is $\delta\langle r^2\rangle/\langle r^2\rangle < 80\times10^{-4}$.

According to Goldstein and Talmi,[3] the $f_{7/2}$ neutron

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