

ions minimized by operating the tube with a low anode voltage, one finds that the yields decrease with decreasing ion energy more rapidly than previously reported. Thus, at least for normal ion incidence, sputtering effects at low ion energy seem to have been overestimated in the past.

3. By extrapolating the lower part of the yield curves, one finds that approximate threshold energies for sputtering are in the range 15 to 45 ev. For argon the product of these thresholds, and the energy transfer factor $4m_1m_2/(m_1+m_2)^2$, is with few exceptions (Pd, U, and Th ~ 15 ev) close to 25 ev which is the energy generally associated with the displacement threshold for radiation damage.⁵ The measurements are presently

being continued and extended to helium and other rare gases.

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¹G. K. Wehner, Advances in Electronics and Electron Physics (Academic Press, Inc., New York, 1955), Vol. 7.

²R. C. Bradley, Phys. Rev. **93**, 119 (1954).

³N. D. Morgulis and V. D. Tischenko, J. Exptl. Theoret. Phys. U.S.S.R. **30**, 54 (1956) [translation: Soviet Phys. JETP **3**, 52 (1956)].

⁴G. K. Wehner, Phys. Rev. **108**, 35 (1957).

⁵G. J. Dienes and G. H. Vineyard, Radiation Effects in Solids (Interscience Publishers, Inc., New York, 1957).

PROPOSAL FOR AN ELECTRON SPIN RESONANCE EXPERIMENT OF S-STATE IONS UNDER HIGH HYDROSTATIC PRESSURE

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The author¹ has shown that a crystal field model gives the cubic field splitting parameter a for Mn^{2+} proportional, to a first approximation, to the square of the cubic crystal field. This reasoning may be extended to ions having the half-closed configuration l^{2l+1} and is explained essentially as follows. Two ions are said to be complementary when the patterns of their linear crystalline Stark splittings are inverted. This is the case for l^x and $l^{2(2l+1)-x}$. Now l^{2l+1} is complementary to itself. If its multiplet were split, it would show two inverted patterns. But since a given multiplet shows only one pattern, any multiplet from l^{2l+1} cannot be split by a linear action of the crystal field. It can be split to the next approximation by the higher order perturbation involving squared off-diagonal elements of the cubic potential. Thus the result may be extended to the l^{2l+1} configuration. The cubic field splitting parameter a would be of the form

$$a = \alpha(D_q)^2 - \beta(D_q)^4, \quad (1)$$

where α and β are constants, and D_q is a measure of the cubic field. In a first approximation only the nearest neighbor ions around the S-state ion considered may be assumed to contribute to

D_q . Thus one obtains

$$D_q = \langle r^4 \rangle (e_1 e_2 / R^5) (1/336) \times \sum_j (35 \cos^4 \theta_j - 30 \cos^2 \theta_j + 3), \quad (2)$$

where $\langle r^4 \rangle$ is the average of r^4 with respect to the radial part of the l orbital; R is the inter-ionic distance between the S-state ion and neighbor ions possessing charges e_1 and e_2 , respectively; θ_j is the azimuth angle of the j th ion with respect to the [001] direction, which is chosen as the z axis of polar coordinates; and j is summed over the nearest ions. It is concluded that the parameter a should be proportional to the inverse tenth power of R and should be positive regardless of the sign of D_q .

Several electron spin resonance (ESR) experiments support this result. Baker, Bleaney, and Hayes² reported that ESR experiments on Mn^{2+} in calcium fluoride yielded

$$a = (+0.6 \pm 0.4) \times 10^{-4} \text{ cm}^{-1}.$$

On the other hand, using $D_q(\text{MgO}) = 4.0 \times D_q(\text{CaF}_2)$ and a for MgO ($a = +18.6 \times 10^{-4} \text{ cm}^{-1}$), they found that from the author's graph¹ of a against D_q that a for CaF_2 should be $\sim +1 \times 10^{-4} \text{ cm}^{-1}$ which is in remarkably good agreement with their value.

Matarresse and Kikuchi⁴ did an ESR experiment on Mn^{2+} in ZnS in which Mn^{2+} is presumed to be surrounded by a tetrahedron of four negative sulfur ions and the sign of D_q would be, therefore, negative. As a result, this system provides an important test for the author's theory. They reported a negative sign for a , which seemed to be inconclusive since this negative sign was determined without measurements of the relative intensities of the transitions at low temperature. Watkins⁵ made such a measurement at 4°K and found that the sign reported was in error. He reported that the sign for a should be positive.

Geschwind⁶ reported that the parameter a for Fe^{3+} is positive in both octahedral and tetrahedral O^{2-} coordination in single crystal of yttrium gallium garnet. Moreover, he re-examined the spectrum of Fe^{3+} in rubidium aluminum sulfate where a negative sign for a was reported earlier,⁷ and found that a is positive in this case also. These results appear to confirm the author's theory.

Recently Low and Rosenburger⁸ have observed the paramagnetic resonance spectra of Gd^{3+} in single crystals of strontium chloride and obtained

a (c in their notation)

$$= (\pm 39.6 \pm 0.1) \times 10^{-4} \text{ cm}^{-1}.$$

On the other hand, Low⁹ reported earlier that a for Gd^{3+} in calcium fluoride is $(+185 \pm 5) \times 10^{-4} \text{ cm}^{-1}$. The ratio of the values of a measured in CaF_2 and $SrCl_2$ is about 4.7. The ratio of the Sr-Cl and Ca-F distances is about 1.28-1.29. Assuming that the trivalent gadolinium ion does not change this ratio appreciably, they calculated the ratio of the values of a in CaF_2 and $SrCl_2$, obtaining about 11.8. This calculated ratio is larger than the experimental one. Thus

they suspect that there may be a mechanism responsible for the splitting being linear in the potential. They also point out that another possibility is to assume that the Gd-Cl or Gd-F distances differ considerably from the Sr-Cl or Ca-F distances.

We wish to call attention to the value of making an ESR experiment on S-state ions under high hydrostatic pressure which reduces the interionic distance R and induces an increase of the parameter a . Such an experiment may provide an important test for the author's theory which predicts an inverse tenth power dependence of a on R . This dependence may be approximately replaced by an inverse ten-thirds dependence on the volume of a single crystal. If this dependence were confirmed, one may calculate the ratio of interionic distances between S-state ions, contained in the host crystal as impurity, and the surrounding ions in various crystals. This ratio may give important information about the host lattice deformation due to impurity ions. On the other hand, if an inverse fifth power dependence were found it would provide an important clue in the investigation of the mechanisms responsible for the splitting parameter a .

¹H. Watanabe, Progr. Theoret. Phys. (Kyoto) **18**, 405 (1957).

²J. Baker, B. Bleaney, and W. Hayes, Proc. Roy. Soc. (London) **A247**, 141 (1958).

³W. Low, Phys. Rev. **105**, 792 (1957).

⁴L. M. Matarrese and C. Kikuchi, J. Phys. Chem. Solids **1**, 117 (1956).

⁵G. D. Watkins, Phys. Rev. **110**, 986 (1958).

⁶S. Geschwind, Phys. Rev. Letters **3**, 207 (1959).

⁷B. Bleaney and R. S. Trenam, Proc. Roy. Soc. (London) **A223**, 1 (1954).

⁸W. Low and U. Rosenburger, Phys. Rev. **116**, 621 (1959).

⁹W. Low, Phys. Rev. **109**, 265 (1958).