[11] M. T. Robinson, Phys. Rev. B 4, 1461 (1971).
[12] B. R. Appleton, S. Datz, C. D. Moak, and M. T. Robinson, Phys. Rev. B 4, 1452 (1971).
[13] F. H. Eisen and M. T. Robinson, Phys. Rev. B 4, 1457 (1971).
[14] M. T. Robinson, Phys. Rev. 179, 327 (1969).

Crystal Field Splitting of Core $p_{3/2}$ Levels*

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The splittings of $p_{3/2}$ atomic core levels due to internal electric field gradients have been calculated for the case of Tm^{3+} ions in thulium ethyl sulphate and shown to be measurable by electron spectroscopy. The splittings could be about 1 eV under favorable conditions.

It has been of great interest for quite some time to know about the effect of environment on the x-ray–emission linewidth in various transition elements. Recently, ESCA measurements[1] on some heavy elements in their compounds showed definite evidence of $p_{3/2}$ level splittings of the order of 10 eV.

We report here the calculations of various $p_{3/2}$ level splittings of thulium ions in thulium ethyl sulphate (TmES). The choice of TmES is due to simplicity of the calculations and the feasibility of comparison of a part of the results obtained here with Mössbauer-effect measurements.[2]

The quadrupolar part of the total Hamiltonian, representing the interaction between a point charge at r, θ, and φ with respect to the nucleus of the ion, and the crystalline electric potential as well as the electric potential due to the crystalline-electric-field- (CEF) split $4f$ unfilled shell could be written[2,3] (assuming axial symmetry of ligands surrounding the rare-earth ion),

$$H_Q = -\left[A_2{}^0 r^2 + \tfrac{1}{4}\langle J\|\alpha\|J\rangle\langle 3J_z{}^2 - J^2\rangle_T K(r)\right](3\cos^2\theta - 1), \tag{1}$$

where

$$K(r) = r^{-3}\int_0^r u_{4f}{}'^2 r'^2\,dr' + r^2\int_r^\infty u_{4f}{}'^2 r'^{-3}\,dr',$$

with $u_{4f}{}'$ the radial part of the $4f$ wave function times r'; $\langle J\|\alpha\|J\rangle$ is the reduced matrix element; $\langle 3J_z{}^2 - J^2\rangle_T$ is the statistical average of matrix elements of the quadrupole operator equivalent between $2J+1$ CEF levels within a manifold of constant $\vec{J}$; and $A_2{}^0$ is the usual parameter in the crystal potential expansion. However, both terms in the interaction Hamiltonian are modified through their effect of polarization on the closed shells (Sternheimer effect[4]). The Sternheimer parameters pertinent to the second term R_{np} have been calculated,[5] whereas those needed for the first term λ_{np} are available in the literature.[3]

The energy splitting of the $np_{3/2}$ level corresponds to the difference in the expectation value of H_Q between the states $|\frac{3}{2}, \pm\frac{3}{2}\rangle$ and $|\frac{3}{2}, \pm\frac{1}{2}\rangle$; after including the Sternheimer effect

$$\Delta E_{np_{3/2}} = \left[A_2{}^0\langle r^2\rangle_{np}(1-\lambda_{np}) + \tfrac{1}{4}\langle J\|\alpha\|J\rangle\langle 3J_z{}^2 - J^2\rangle_T\langle K(r)\rangle_{np}(1-R_{np})\right] \times\langle\tfrac{3}{2}\|\alpha\|\tfrac{3}{2}\rangle\left(\langle\tfrac{3}{2}|3J_z{}^2 - J^2|\tfrac{3}{2}\rangle - \langle\tfrac{1}{2}|3J_z{}^2 - J^2|\tfrac{1}{2}\rangle\right). \tag{2}$$

Confining our attention to the ${}^3H_6$ term of the ground multiplet of TmES, we have evaluated $A_2{}^0 \equiv C_2{}^0/\langle r^2\rangle_{4f}(1-\lambda_{4f})$, where $C_2{}^0 = 130.5\ \mathrm{cm}^{-1}$ is obtained by Barnes *et al.*[2] from the optical measurements of Wong and Richman,[6] and $\langle r^2\rangle_{4f} \times(1-\lambda_{4f}) = 0.282$.[3] $\langle J\|\alpha\|J\rangle = 1.02\times10^{-2}$; $\langle 3J_z{}^2 - J^2\rangle_T$ are calculated using Table IV of Ref. 2. The factor outside the square bracket is $\frac{4}{5}$. The R_{np} and $\langle K(r)\rangle_{np}$ pertinent to the present work

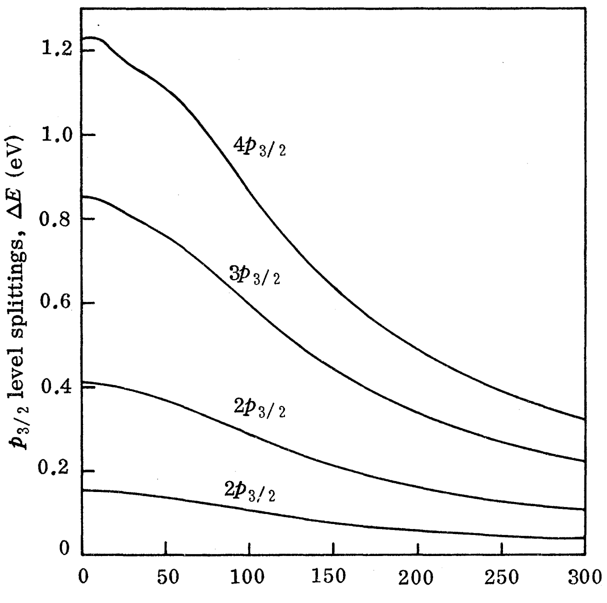

FIG. 1. Temperature dependence of $p_{3/2}$ level splittings of Tm^{3+} ions in TmES after ignoring the crystal-potential term in Eq. (2).

have been calculated using the technique suggested in Ref. 3. These are $R_{2p}=0.194$, $R_{3p}=0.171$, $R_{4p}=0.172$, $R_{5p}=0.142$, $\langle K(r)\rangle_{2p}=0.089$, $\langle K(r)\rangle_{3p}=0.474$, $\langle K(r)\rangle_{4p}=0.689$, and $\langle K(r)\rangle_{5p}=0.222$.

The results are plotted in Fig. 1, which shows the splittings of various $p_{3/2}$ levels in the temperature range of interest. The crystal-potential term contributes less than 2% to the total splitting except in the $5p_{3/2}$ case where its contribution is 0.102 eV. This is in contrast to the case of Mössbauer-effect measurements on nuclear energy-level splittings where the crystal-potential contribution could be comparable with the potential due to the $4f$ shell. Present investigation thus suggests that the crystal-field effects on core energy levels are not negligible and could be large in transition-element salts and heavy-element compounds where the valence shells are directly exposed to the crystal field. We are working out the $p_{3/2}$ level splittings in various ions of interest to experimentalists and the results will be published elsewhere.

We now compare the accuracy of our calculations of various Sternheimer parameters with the available measurements. Barnes *et al.* obtained $\rho \equiv (1-\lambda_{\mathrm{nucl}})/(1-R)(1-\lambda_{4f})=287$ for Tm^{3+} in TmES assuming $Q=1.5$ b for the 8.4-keV excited state of Tm^{169}. We have calculated R using the unified approach for the calculation of the R_{np} and λ_{np} and found $R=0.181$.[7] $\lambda_{\mathrm{nucl}}=-72.9$ and $\lambda_{4f}=0.601$ were calculated in a previous work.[3] We thus obtain $\rho=226$. With the better computational facilities now available it could be hoped that the calculation of Sternheimer shielding and antishielding parameters might be reliable enough to get the quadrupole moment of the nuclei by Mössbauer spectroscopy coupled with ESCA measurements.

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[1] T. Novakov and J. M. Hollander, Phys. Rev. Lett. 21, 1133 (1968), and Bull Amer. Phys. Soc. 10, 597 (1969). ESCA: electron spectroscopy for chemical analysis.

[2] R. G. Barnes, E. Kankeleit, R. L. Mössbauer, and J. M. Poindexter, Phys. Rev. Lett. 11, 253 (1963), and Phys. Rev. 136, A175 (1964).

[3] R. P. Gupta, B. K. Rao, and S. K. Sen, Phys. Rev. A 3, 545 (1971).

[4] R. M. Sternheimer, Phys. Rev. 80, 102 (1950), and 105, 158 (1957), and 146, 140 (1966).

[5] The details of calculations and the values of R_{nl} for Pr^{3+}, Tm^{3+}, W^{+}, and Au^{+} will be reported elsewhere.

[6] E. Y. Wong and I. Richman, J. Chem. Phys. 34, 1182 (1961).

[7] $R=0.118$ for Pr^{3+}, -0.418 for W^{+}, and -1.776 for Au^{+} have also been calculated.