

NOTE

Crystal Field Energy Levels and State Vectors for the $3d^N$ Ions at Orthorhombic or Higher Symmetry Sites

The transition-metal $3d^N$ ions are well known to play an important role in physics and chemistry of materials [1, 2]. In particular, the knowledge of the energy levels and state vectors, which are characterized by the *crystal field* (CF) or *ligand field* parameters, should enable people to understand the spectroscopic and magnetic properties of a wide variety of paramagnetic crystals. This requires a way to correlate the optical spectroscopy data [3] with electron paramagnetic resonance (EPR) data as well as Mössbauer spectroscopy and magnetic susceptibility data. Our recent literature survey focused on $3d^4$ and $3d^6$ ions has revealed numerous cases of Fe^{2+} ($3d^6$) ions with high-spin $S=2$ at the orthorhombic as well as the tetragonal symmetry sites. Several pertinent cases of the $3d^4$ (Cr^{2+} , Mn^{3+} , Fe^{4+}) and $3d^6$ (Co^{3+}) ions have also been identified. The splittings of the ground 4A_2 and excited 2E states for the Cr^{3+} ($3d^3$) ion at noncubic sites in MgO have recently been studied [4–5] using full diagonalization of a non-cubic CF Hamiltonian with CF parameters derived from the data on the strain-induced splittings of Cr^{3+} doped in Al_2O_3 [6].

In this note, we report the availability of a computer program (and its future development) for simulation and analysis of the experimental data on the energy levels and state vectors for the $3d^N$ ions, $N=1$ to 9, using the crystal-field approach which involves full diagonalization within the $3d^N$ configuration of a complete Hamiltonian including electrostatic terms, Trees correction, spin-orbit interaction, and crystal-field. At present no such program is available in the public domain for general usage. Hence, individual researchers have either to spend a lot of time in developing their own programs in mainframe computer (see, e.g., Ref. [7] for a program applicable to tetragonal symmetry only) or to rely on the Tanabe–Sugano ligand field diagrams (see Ref. [8] for detailed tabulation) for partial information also pertinent to axial symmetry only. In order to rectify the situation we have recently undertaken a systematic development of a computer package for crystal field analysis within the whole $3d^N$ configuration ($N=2$ to 8) and for symmetry as low as orthorhombic [9].

The present version of the CF analysis computer program is an extension of the previous one [9]. It includes for completeness the cases of the $3d^1$ and $3d^9$ configuration and,

moreover, a new program recently constructed using the $|d^N\alpha SLJM_J\rangle$ basis of state which complements the original one using the $|d^N\alpha SM, LM\rangle$ basis. Both programs are suitable for orthorhombic symmetry (point groups: D_2 , C_{2v} , D_{2h}) and due to the ascent in symmetry method for tetragonal symmetry (point groups: D_4 , C_{4v} , D_{2d} , D_{4h}) as well as cubic symmetry (point groups: T , T_h , O , T_d , O_h). Separately trigonal symmetry (point groups: D_3 , C_{3v} , D_{3d}) and hexagonal symmetry (point groups: C_6 , C_{3h} , C_{6h} , D_6 , C_{6v} , D_{3h} , D_{6h}) have also been considered. Besides, a special emphasis has been placed on applications to $3d^4$ and $3d^6$ ions in crystals. For this purpose our general computer programs have been modified and a well-documented manual has been worked out [10] to enable studies of the 5D approximation and (5D and 3F_i) approximation, in addition to the full diagonalization within the $3d^4$ or $3d^6$ configuration. Currently our work concentrates on an extension to monoclinic and triclinic, as well as to trigonal and tetragonal symmetry cases involving “imaginary” CF terms, which has just been developed and is undergoing final tests. Application to some C_3 symmetry cases are now in progress.

In essence, our program can construct and diagonalize the Hamiltonian matrix for an iron group ion within the whole d^N configuration, which includes the following contributions (for details, see Refs. [3, 11, 12])

$$\mathcal{H} = \mathcal{H}_f + \mathcal{H}_{CF} = \mathcal{H}_{es} + \mathcal{H}_{so} + \mathcal{H}_{Trees} + \mathcal{H}_{CF}, \quad (1)$$

where the free-ion Hamiltonian \mathcal{H}_f (excluding the kinetic energy of electrons and their Coulomb attraction with nucleus) consists of the electrostatic repulsion \mathcal{H}_{es} amongst these $3d$ electrons, the spin-orbit interaction \mathcal{H}_{so} , and the Trees correction \mathcal{H}_{Trees} describing the two-body orbit–orbit polarization interaction [11]. Explicit forms of \mathcal{H}_{es} , \mathcal{H}_{so} , and \mathcal{H}_{Trees} and formulas for evaluating their matrix elements can be found in Ref. [9]. As a typical example to illustrate our computational methodology, we shall give more details on the crystal field Hamiltonian (in Wybourne's notation [12])

$$\mathcal{H}_{CF} = \sum_{kq} B_{kq} C_q^{(k)}, \quad (2)$$

where B_{kq} are the crystal field parameters representing the $3d$ electron radial integral and the crystal field interaction strength and $C_q^{(k)}$ are the renormalized spherical tensor operators of the $3d$ electron angular momenta. Conversion relations between B_{kq} defined in (2) and other CF parameter notations have been provided in [9].

In the LS coupling scheme for intermediate crystal field strength, the basis of states is taken as

$$|\psi\rangle = |d^N \alpha S M_S L M\rangle, \quad (3)$$

where α is an extra quantum number (seniority) and the orbital quantum number $l = d = 2$. Hence the matrix elements of the crystal field Hamiltonian (2) are evaluated as

$$\begin{aligned} \langle \psi | \mathcal{H}_{CF} | \psi' \rangle &= \sum_{kq} B_{kq} (-1)^{L-M} \begin{pmatrix} L & k & L' \\ -M & q & M' \end{pmatrix} \\ &\times \langle \beta \| C^{(k)} \| \beta' \rangle \delta_{SS'} \delta_{M_S M_S'}, \end{aligned} \quad (4)$$

where $\beta \equiv d^N \alpha L S$ and

$$\langle \beta \| C^k \| \beta' \rangle = (-1)^d (2d+1) \begin{pmatrix} d & k & d \\ 0 & 0 & 0 \end{pmatrix} \langle \beta \| U^k \| \beta' \rangle.$$

The reduced matrix elements for the unit tensor operator U^k (and those operators involved in \mathcal{H}_{es} and \mathcal{H}_{so}) have been calculated [9] for each $3d^N$ configuration using the tensor operator techniques [12], together with the recoupling coefficients and the coefficients of fractional parentage [13]. Those calculated matrix elements are stored in some data files to save computing effort for recalculation. The $3-j$ symbols (\dots) are evaluated by a subroutine in the library, AtomLib.Lib, developed by Y. Y. Yeung for general matrix manipulations (including solutions of eigenproblems) and for calculating the atomic coefficients such as the $3j$, $6j$, and $9j$ symbols. The crystal field analysis package, HCFLDN, has been developed specifically for a personal computer (IBM 286 PC or compatible) and it consists of a program with numerous subroutines, a library, and supplementary data files which can be edited or modified by the users. For technical details, file organization, flow chart, and input/output specifications, we refer to Ref. [9]. A new program, HCFJDN, constructed using an alternative basis of state, namely $|\psi\rangle = |d^N \alpha S L J M_J\rangle$, has also been developed. The matrix elements for the terms \mathcal{H}_{es} and \mathcal{H}_{Tees} in the new basis depend on the quantum numbers $\alpha S L$ only, like those in the $|d^N \alpha S M_S L M\rangle$ basis but the matrix elements for the terms \mathcal{H}_{so} and \mathcal{H}_{CF} are very different and some new subroutines have been specifically written for the program HCFJDN (see Ref. [12] for the details of the tensor operator techniques involved). In general, the program HCFJDN yields an identical set of eigenvalues as the

program HCFLDN. However, the alternative eigenvectors are entirely different and they would be more appropriate for the $3d^N$ ions in very weak CF cases and especially when calculations in a limited basis of states are to be carried out.

The input data for both programs, HCFLDN and HCFJDN, includes five free ion parameters, namely, A , B , and C for \mathcal{H}_{es} , α for \mathcal{H}_{Tees} , and ζ for \mathcal{H}_{so} , as well as the crystal field parameters B_{kq} . Supplementary data files are also required for the reduced matrix elements of the incurring tensor operators and the state labels as mentioned above. The output is stored in a file containing the sequential numbers as well as quantum numbers of all $|\alpha S M_S L M\rangle$ (or $|\alpha S L J M_J\rangle$) states used, a selected set of eigenvalues and eigenvectors for all states, or any number of the low-lying states and a complete set of energies sorted in ascending order. The intermediate results can be directed either to the screen or to a printer for monitoring purposes. Some physical applications, advantages, and further development of our present computer package are briefly outlined below.

(1) The energy levels calculated within the whole $3d^N$ configuration are much more accurate and reliable than the conventional truncated basis approximation often used in analyzing the optical spectra of $3d^N$ ions. For example, the CF analysis of the $3d^4$ and $3d^6$ ions at orthorhombic symmetry has recently been worked out [14] within the 5D term approximation. However, our recent calculations [10] using the present computer package indicate that the 5D approximation is not satisfactory for the case of strong orthorhombic CF components (relative to the cubic ones). This is because the orthorhombic CF induces strong mixing of states arising from some high-lying levels (especially 3F_i states of the 3P , 3F , 3G , and 3H terms) as revealed from our results of full diagonalization within the whole $3d^4$ or $3d^6$ configuration. Furthermore, the tremendous effort to make systematic and lengthy tabulation of the energy levels for the $3d$ ions at various possible hosts [15], which gives some very valuable information although it provides very limited state vector coefficients, could now be avoided since all the necessary information can be readily provided or supplemented (for the cases not available in the literature) by our computer package, together with a concise table of the relevant CF parameters.

(2) Using our computer package (earlier version), the ground and low-lying level splittings of $Cr^{3+} : MgO$ have been successfully correlated [4, 5] with the local non-cubic distortion induced by Cr^{3+} doped at the cation site with a nearby charge-compensating vacancy. The conventional perturbation approach (up to fourth order) for the energy splitting of the first excited 2E state of Cr^{3+} yielded [4] the value 157 cm^{-1} which was in large discrepancy with the measured one of 93.5 cm^{-1} , whereas our result calculated from the full diagonalization of the complete CF Hamiltonian yielded the value 94.1 cm^{-1} . The reason can

be ascribed to the large effect of non-cubic CF induced mixing of nearby states which makes the perturbational series to either diverge or converge too slowly.

(3) Using the coefficients of the CF state vectors, the EPR spectra of the zero-field splitting of some $3d$ ions with orbital singlet ground state (e.g., 4A_2 of Cr^{3+} and ${}^6S_{5/2}$ of Mn^{2+}) can be correlated with the optical spectra and explained by the same set of parameters. As a successful example, the spin Hamiltonian parameters for the strain-induced splitting of the 4A_2 state in $\text{Cr}^{3+}:\text{Al}_2\text{O}_3$ have been expressed in terms of the superposition model intrinsic parameters [6] describing the optical spectra. Satisfactory agreement between theoretical and experimental results has been achieved since the calculated values were lying mostly within the experimental uncertainties of the measured data when the four intrinsic parameters were fitted [6] to the data set of 11 spin Hamiltonian parameters.

(4) Accurate CF state vector coefficients are also required to evaluate the expectation values (with respect to various CF states) of the magnetic moment operator

$$\mathbf{m} = \mu_B(k\mathbf{L} + g_e\mathbf{S})$$

where μ_B is the Bohr magneton, k the Stevens orbital reduction factor, and $g_e = 2.0023$. The expectation values are directly related to the spectroscopic splitting g -factor for quantifying the Zeeman effect and for identifying various energy levels by polarization. Currently, it is of great interest [16, 17] to obtain quantitatively the relative intensities of the $3d^N$ intra-configurational one-photon, two-photon, and even n -photon transitions of which the associated intensity parameters have so far been treated as phenomenological parameters to be adjusted with experimental data. Hence, we intend to extend our package to predict the static paramagnetic susceptibility χ and the oscillator strength, as well as the absorption cross sections and radiative lifetimes for the magnetic dipole-induced transition for any $3d$ ion in crystals. For this purpose, a new program is currently being developed in conjunction with the existing package to deal with the related computational work.

A copy of the present computer package with a user's document is obtainable from one of us (Y. Y. Yeung) by sending a high density diskette and an address label.

ACKNOWLEDGMENTS

Financial support from University and Polytechnic Grants Committee and the City Polytechnic of Hong Kong as well as Hong Kong Polytechnic Research Subcommittee is gratefully acknowledged.

REFERENCES

1. See, for example, A. B. P. Lever, *Inorganic Spectroscopy*, 2nd ed. (Elsevier, Amsterdam, 1984).
2. C. A. Morrison, *Crystal Fields for Transition-Model Ions in Laser Host Materials* (Springer-Verlag, Berlin, 1992).
3. S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals* (Academic Press, New York, 1973).
4. Y. Y. Yeung, *J. Phys.: Condens. Matter* **2**, 2461 (1990).
5. T. L. Choy and Y. Y. Yeung, *Phys. Status. Solidi B* **161**, K107 (1990).
6. Y. Y. Yeung and D. J. Newman, *Phys. Rev. B* **34**, 2258 (1986).
7. M. L. Ellzey, *Comput. Phys. Commun.* **10**, 133 (1975).
8. E. König and S. Kremer, *Ligand Field Energy Diagrams* (Plenum Press, New York, 1977).
9. Y. Y. Yeung and C. Rudowicz, *Comput. & Chem.* **16**, 207 (1992).
10. C. Rudowicz, Y. Y. Yeung, M. L. Du, and Y. M. Chang, Research Report AP-92-29, City Polytechnic of Hong Kong, Hong Kong, 1992.
11. M. Gerloch and R. C. Slade, *Ligand Field Parameters* (Cambridge, Univ. Press, London, 1973).
12. B. G. Wybourne, *Spectroscopic Properties of Rare-Earth* (Wiley, New York, 1965).
13. C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for p^n , d^n and f^n Configurations* (MIT Press, Cambridge, MA, 1964).
14. C. Rudowicz, Y. Y. Zhou, and W. L. Yu, *J. Phys. Chem. Solids* **53**, 1227 (1992).
15. See, for example, C. A. Morrison, Harry Diamond Laboratories Report HDL-TM-91-1, 1991 (unpublished).
16. M. Kibler and J. C. Gacon, *Croat. Chem. Acta* **62**, 783 (1989).
17. J. Sztucki and W. Strek, *Chem. Phys.* **143**, 347 (1990).

Received July 8, 1992; revised January 27, 1993

Y. Y. YEUNG

Department of Applied Physics
Hong Kong Polytechnic
Hungghom, Hong Kong

C. RUDOWICZ

Department of Applied Science
City Polytechnic of Hong Kong
Kowloon, Hong Kong