THE JOURNAL OF CHEMICAL PHYSICS **140**, 167101 (2014)

Comment on "Effective field parameters in iron Mössbauer spectroscopy" [J. Chem. Phys. 47, 961 (1967)]

W. N. Rowan-Weetaluktuk,[1] J. M. Cadogan,[2] and D. H. Ryan[1]
[1]*Physics Department and Centre for the Physics of Materials, McGill University, 3600 University Street, Montreal, Quebec H3A 2T8, Canada*
[2]*School of Physical, Environmental and Mathematical Sciences, UNSW Canberra at the Australian Defence Force Academy, Canberra, ACT 2610, Australia*

(Received 4 December 2013; accepted 25 March 2014; published online 22 April 2014)

[http://dx.doi.org/10.1063/1.4871464]

While the Mössbauer spectrum of a magnetically ordered powder sample can be used to determine the direction of the local hyperfine field (B_{hf}) in the coordinate system defined by the electric field gradient (efg) tensor, the spectrum of an oriented single-crystal provides a direct measurement of the angle between the absorbed or emitted γ and B_{hf}, primarily through the observed line intensities. Several solutions to the general static Mössbauer problem for M1 transitions (relevant for the two most commonly used Mössbauer isotopes: ^{57}Fe and ^{119}Sn) have been published,[1–3] and all can be adapted to computer code to fit the relevant experimental variables. Unfortunately there is an error in Eq. (12) from Hoy and Chandra[2] and both the sign of the last term and the sign of the exponent in the last term are incorrect. For single-crystal samples, this leads to a severe mis-calculation of line intensities when the angle (θ) between B_{hf} and the principal axis of the efg tensor (V_{zz}) is non-zero, and so code based on this expression (see, for example, Ref. 4) gives incorrect fits.

Starting from Eq. (11) of Hoy and Chandra[2] for the intensity, $I(\Lambda_i^e \leftrightarrow \Lambda_j^g)$, of the transition between the excited state, Λ_m^e, and ground state, Λ_m^g:

$$\begin{aligned} I\left(\Lambda_i^e \leftrightarrow \Lambda_j^g\right) = \Big| & a_{i1}b_{j1}^* \left\langle \tfrac12 1 \tfrac12 1 \middle| \tfrac32 \tfrac32 \right\rangle \chi_1^1 \\ & + a_{i2}b_{j1}^* \left\langle \tfrac12 1 \tfrac12 0 \middle| \tfrac32 \tfrac12 \right\rangle \chi_1^0 \\ & + a_{i3}b_{j1}^* \left\langle \tfrac12 1 \tfrac12 -1 \middle| \tfrac32 \tfrac{-1}{2} \right\rangle \chi_1^{-1} \\ & + a_{i2}b_{j2}^* \left\langle \tfrac12 1 \tfrac{-1}{2} 1 \middle| \tfrac32 \tfrac12 \right\rangle \chi_1^1 \\ & + a_{i3}b_{j2}^* \left\langle \tfrac12 1 \tfrac{-1}{2} 0 \middle| \tfrac32 \tfrac{-1}{2} \right\rangle \chi_1^0 \\ & + a_{i4}b_{j2}^* \left\langle \tfrac12 1 \tfrac{-1}{2} -1 \middle| \tfrac32 \tfrac{-3}{2} \right\rangle \chi_1^{-1} \Big|^2, \end{aligned} \tag{1}$$

where a_{ij} and b_{ij} are the (i,j) elements of the Hamiltonian of the excited and ground states, respectively, $\langle I_g l m_g m | I_e m_e \rangle$ are the Clebsch-Gordon coefficients, and χ_l^m are the vector spherical harmonics[5] which obey the parity relation $\chi_l^m = (-1)^m \chi_l^{-m*}$. Defining

$$A = a_{i1}b_{j1}^* + \sqrt{\frac{1}{3}}a_{i2}b_{j2}^*, \tag{2a}$$

$$B = \sqrt{\frac{2}{3}}\left(a_{i2}b_{j1}^* + a_{i3}b_{j2}^*\right), \tag{2b}$$

$$C = a_{i4}b_{j2}^* + \sqrt{\frac{1}{3}}a_{i3}b_{j1}^*, \tag{2c}$$

then substituting A, B, and C into Eq. (1), and expanding give

$$\begin{aligned} I\left(\Lambda_i^e \leftrightarrow \Lambda_j^g\right) = {} & |A|^2\left|\chi_1^1\right|^2 + |B|^2\left|\chi_1^0\right|^2 + |C|^2\left|\chi_1^{-1}\right|^2 \\ & +2Re\left[AB^*\chi_1^1\chi_1^{0*}\right] + 2Re\left[AC^*\chi_1^1\chi_1^{-1*}\right] \\ & +2Re\left[BC^*\chi_1^0\chi_1^{-1*}\right]. \end{aligned} \tag{3}$$

The relevant χ_l^m dot products[6] are

$$\left|\chi_1^1\right|^2 = \left|\chi_1^{-1}\right|^2 = 1 + \cos^2\theta, \tag{4}$$

$$\left|\chi_1^0\right|^2 = 2\sin^2\theta, \tag{5}$$

$$\chi_1^1\chi_1^{0*} = -\chi_1^0\chi_1^{-1*} = \sqrt{2}\,e^{i\phi}\sin\theta\,\cos\theta, \tag{6}$$

$$\chi_1^1\chi_1^{-1*} = e^{2i\phi}\sin^2\theta, \tag{7}$$

where θ and ϕ denote the polar and azimuthal angles, respectively, of the absorbed γ with respect to the principal axis of the electric field gradient. The error propagating from the original work[2] was introduced in the dot product terms represented by Eq. (6) above. Substituting the χ_l^m products into Eq. (3) gives

$$\begin{aligned} I\left(\Lambda_i^e \leftrightarrow \Lambda_j^g\right) = {} & (|A|^2 + |C|^2)(1+\cos^2\theta) + |B|^2 2\sin^2\theta \\ & +2Re[AB^*\sqrt{2}\,e^{i\phi}\sin\theta\,\cos\theta] \\ & +2Re[AC^*e^{2i\phi}\sin^2\theta] \\ & -2Re[BC^*\sqrt{2}\,e^{i\phi}\sin\theta\,\cos\theta]. \end{aligned} \tag{8}$$

This confirms the expression for the intensity from Voyer and Ryan.[3] It should be noted that the powder solution provided by Hoy and Chandra[2] is correct, however single-crystal code developed using the Hoy and Chandra[2] intensity expression will provide inconsistent values for the hyperfine parameters.

This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada, and Fonds Québécois de la Recherche sur la Nature et les Technologies. J.M.C. is supported by The University of New South Wales and the Australian Research Council.

[1] W. Kündig, Nucl. Instrum. Methods **48**, 219 (1967).
[2] G. R. Hoy and S. Chandra, J. Chem. Phys. **47**, 961 (1967).
[3] C. J. Voyer and D. H. Ryan, Hyperfine Interact. **170**, 91 (2006).
[4] A. P. Douvalis, A. Polymeros, and T. Bakas, J. Phys.: Conf. Ser. **217**, 012014 (2010).
[5] J. Jackson, *Classical Electrodynamics*, 3rd ed. (Wiley, 1999), p. 431.

[6] For clarity, a common pre-factor of $\frac{3}{16\pi}$ has been omitted from Eqs. (4)–(8).