Reexamination of the Mössbauer Isomer Shift*

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Reexamination of the isomer shift has led us to propose that the phonons in a lattice change the electron density at the site of the resonant nucleus, thereby causing a change in the energy of the emitted γ photon in the recoilless emission of radiation. The new shift is highly temperature dependent and is significantly smaller than the well-known isomer shift. Experimental evidence is presented.

THE lattice vibrations in solids are known to cause a Stark analog,[1] a shift in electron spin resonance,[2,3] a shift in nuclear magnetic resonance,[4] and a shift in zero-phonon optical absorption.[5] In this paper we propose that the excitation of electrons by phonons changes the electron density at the site of the nucleus, thereby leading to a change in the energy of the emitted photon in Mössbauer resonance. The relativistic decrease of mass of the emitting nucleus in a system of coupled oscillators increases the frequencies of all normal modes of the system which do not have a node at the site of the changed mass and the corresponding increase in the internal energy requires that the energy of the emitted photon be decreased.[6,7] Another shift, occurring essentially because of the difference δr between the radius of the resonant nucleus before and after the emission and because of a finite electron density at the site of the nucleus, appears as[8,9]

$$\Delta S^{(i)}=\frac{4\pi Ze^2cr\delta r}{5E_\gamma}|\Psi(0)|^2, \tag{1}$$

where Ze is the nuclear charge, r is the nuclear radius, and $\Psi(0)$ is the electronic wave function evaluated at the site of the nucleus which we investigate in detail.

Consider an Fe^{3+} in an octahedral environment of fluoride[9] ions. The pertinent wave functions are

$$\Psi_{z^2a}=N_{z^2a}(\Psi_{z^2}-\lambda_s\chi_s-\lambda_\sigma\chi_\sigma), \tag{2}$$

$$\Psi_{z^2b}=N_{z^2b}(\chi_k+\gamma_k\Phi_{z^2}), \tag{3}$$

where Φ_{z^2} is the one-electron d function on the iron, and $\chi_k(k=s,\sigma)$ represents a linear combination of F^- one-electron functions transforming like the E_g irreducible representation of the octahedral group. The amplitudes of (2) and (3) at the site of the iron nucleus are negligibly small so that they do not contribute to (1). The main contribution to (1) arises from the core s functions, which we write as

$$\Phi_{ns}=N_{ns}(\phi_{ns}-\sum_k\alpha_{nk}\xi_k), \tag{4}$$

$$\zeta_k=N_k(\xi_k+\sum_n\beta_{nk}\phi_{ns}), \tag{5}$$

where

$$\alpha_k=S_{nsk}+\beta_{nk},$$

$$N_{ns}=(1-2\sum_k\alpha_{nk}S_{nsk}+\sum_k\alpha_{nk}^2)^{-1/2},$$

and $S_{nsk}=\langle\phi_{ns}|\xi_k\rangle$ is the group overlap integral, ξ_k are the ligand F^- functions suitably combined to transform like A_{1g} of the cubic group. The contribution of (4) to the electron density at the site of the resonant nucleus is

$$\sum_n|\phi_{ns}(0)|^2(1-\sum_k\alpha_{nk}^2)^{-1}\simeq\sum_n|\phi_{ns}(0)|^2(1+\sum_k\alpha_{nk}^2),$$

and that of (5) is

$$\sum_{nk}\beta_{nk}^2|\phi_{ns}(0)|^2,$$

so that

$$\sum_n|\Psi_{ns}(0)|^2\simeq\sum_n|\phi_{ns}(0)|^2(1+\sum_k\alpha_{nk}^2+\sum_k\beta_{nk}^2).$$

The ϕ_{ns} are doubly occupied so that a proper summation on all the spin-polarized orbitals[10] gives[11]

$$\Delta S^{(i)}=\frac{4\pi Ze^2cr\delta r}{5E_\gamma}\sum_n\{|\phi_{ns\uparrow}(0)|^2+|\phi_{ns\downarrow}(0)|^2\}[1+\sum_k(\alpha_{nk}^2+\beta_{nk}^2)], \tag{6}$$

where we assumed $\alpha_{nk\downarrow}=\alpha_{nk\uparrow}$ and $\beta_{nk\downarrow}=\beta_{nk\uparrow}$.

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[1] K. N. Shrivastava, Phys. Rev. **187**, (1969).
[2] K. N. Shrivastava, Proc. Phys. Soc. (London) **C2**, 777 (1969).
[3] W. M. Walsh, Jr., J. Jeener, and N. Bloembergen, Phys. Rev. **139**, A1338 (1965).
[4] K. N. Shrivastava, Bull. Am. Phys. Soc. **14**, 835 (1969).
[5] K. N. Shrivastava, Proc. Phys. Soc. (London) **C2**, 2428 (1969); G. F. Imbush, W. M. Yen, A. L. Schawlow, D. E. McCumber, and M. D. Sturge, Phys. Rev. **133**, A1029 (1964).
[6] B. D. Josephson, Phys. Rev. Letters **4**, 331 (1960). See also, R. V. Pound and G. A. Rebka, *ibid.* **4**, 275 (1960); J. P. Schiffer, P. V. Parks, and J. Heberle, Phys. Rev. **133**, 1553 (1964).
[7] A very good account of the second-order Doppler shift is given by A. A. Maradudin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18, p. 273.
[8] O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters **4**, 412 (1960).
[9] L. R. Walker, G. K. Wertheim and V. Jaccarino, Phys. Rev. Letters **6**, 98 (1961).
[10] J. H. Wood and G. W. Pratt, Jr., Phys. Rev. **107**, 995 (1957).
[11] For the present purpose one can ignore the difference between the two polarized orbits within the "desired accuracy" but we have written (6) so as to save the analogy with the Knight shift. It may be mentioned that the Knight shift and the isomer shift are by no means related.

Now the phonon-excitation included in (2) with the known methods[2,12] gives

$$\Psi_{z^2}''=N_{z^2}''(\Phi_{z^2}-\sum_k \lambda_k\chi_k-\mu_{sz^2}'\phi_{ns}),$$
$$\Psi_{x^2-y^2}''=N_{z^2}''(\Phi_{x^2-y^2}-\sum_k \lambda_k\chi_k-\mu_{s(x^2-y^2)}'\phi_{ns}), \quad (7)$$

where we have omitted certain terms[2] which are not important for the present purpose. The function (4) becomes

$$\Phi_{ns}''=N_{ns}''(\phi_{ns}-\sum_k \alpha_{nk}\xi_k-\alpha_{nk}'\xi_k), \quad (8)$$

with

$$\mu_{sz^2}'=\sum_k a_{nsk}(2\epsilon_{zz}-\epsilon_{xx}-\epsilon_{yy})/\sqrt{3},$$
$$\mu_{s(x^2-y^2)}'=\sum_k a_{nsk}(\epsilon_{xx}-\epsilon_{yy}),$$
$$\alpha_{nk}'=\sum_k z_{nsk}\epsilon_{00},$$

where

$$a_{nsk}=-R(\partial/\partial R)(\lambda_k S_{nsk}),$$
$$z_{nsk}=-R(\partial/\partial R)(S_{nsk}-\alpha_{nk}),$$

and ϵ_{ij} are the dynamic strains.[12] Apart from (6), the functions (7) and (8) give a new shift,

$$\Delta S^{\text{new}}=\frac{4\pi Ze^2cr\delta r}{5E_\gamma}\sum_n\{|\phi_{ns\uparrow}(0)|^2+|\phi_{ns\downarrow}(0)|^2\}\times(\mu_{sz^2}'^2+\mu_s{}^2{}_{(x^2-y^2)}'+\alpha_{sz^2}'^2),$$

which arises essentially because of phonon excitation and indicates that the energy of the γ ray emitted in a Mössbauer resonance is changed by the electron-phonon interaction. Making the usual approximations[12] in the Debye model, we find

$$\Delta S^{\text{new}}=\frac{4\pi Ze^2cr\delta r}{25E_\gamma}\sum_n\{|\phi_{ns\uparrow}(0)|^2+|\phi_{ns\downarrow}(0)|^2\}\times(2a_{nss}{}^2+2a_{ns\sigma}{}^2+z_{nss}{}^2+z_{ns\sigma}{}^2)(\hbar/\rho\pi^2)(v_t{}^{-5}+\tfrac{2}{3}v_l{}^{-5})\times(k/h)^4\left(\tfrac{1}{8}\Theta^4+T^4\int_0^{\Theta/T}\frac{x^3dx}{e^x-1}\right), \quad (9)$$

where ρ is the mass density of the crystal, v_t and v_l are the transverse and longitudinal sound velocities, and Θ is the Debye characteristic temperature. It is known from the experimental work of Pound *et al.*[13] that (1) is a function of volume for ^{57}Fe in Fe at room temperature. We believe that our expression (6) provides the first theoretical explanation of such a volume dependence because the quantities α_{nk} are very sensitive functions of the separation between the resonant ^{57}Fe and its nearest neighbor. The measurements of the center shift by Preston *et al.*[14] and Steyert and Taylor[14] for ^{57}Fe in several environments have failed to show a temperature dependence of the isomer shift, thus suggesting that the shift does not depend on the volume, which is contrary to the work of Pound *et al.*[13] In order to make the experiments of Pound *et al.* consistent with those of Preston *et al.*, we suggest that as the volume is increased (keeping the temperature constant), the overlaps in (6) decrease. This would explain the work of Pound *et al.* However, as the temperature increases the amplitudes of the vibrating ions are increased and there occurs a net increase, given by (9). Thus the termal expansion and the harmonic lattice vibrations work in opposite directions, cancelling the effect of each other in the particular cases studied by Preston *et al.* and Steyert and Taylor. We therefore believe that our new shift (9) has actually been observed in the experiments.[14,15] Approximate estimates using the Hartree-Fock wave functions[16] and typical values $\rho\simeq 3$ g/cm^3, $v_t\simeq v_l\simeq 5\times10^{15}$ cm/sec and $\Theta\simeq 500$°K suggest that

$$\Delta S^{\text{new}}/\Delta S^{(i)}\simeq 0.002+2\times10^{-13}T^4\int_0^{\Theta/T}\frac{x^3dx}{e^x-1}. \quad (10)$$

At 300°K the second term in (10) is computed to be 1.6×10^{-3}. The exact calculations for ^{57}Fe in Fe will be very complicated if not impossible, yet, we propose that the possibility of (9) should be considered in experiments which measure the temperature dependence in the isomer shift.[17]

[12] J. H. Van Vleck, Phys. Rev. **57**, 426 (1940); R. Orbach and P. Pincus, *ibid.* **143**, 168 (1966).

[13] R. V. Pound, G. Benedek, and R. W. P. Drever, Phys. Rev. Letters **7**, 405 (1961).

[14] R. S. Preston, S. S. Hanna, and J. Heberle, Phys. Rev. **128**, 2207 (1962); W. A. Stevert and R. D. Taylor, *ibid.* **134**, A716 (1964).

[15] Recently, R. D. Taylor and E. K. Storms [Bull. Am. Phys. Soc. **14**, 836 (1969)] have done interesting experiments on W and Ta in which the observed temperature dependence is much larger than can be understood on the basis of known second-order Doppler shift. We believe that this is experimental evidence supporting the existence of (9). In contrast to the behavior of ^{57}Fe (Ref. 14), in W apparently the effect of harmonic vibrations does not completely cancel the effect of lattice expansion.

[16] R. E. Watson, Technical Report No. 12, Solid State and Molecular Theory Group, M.I.T., 1959 (unpublished); C. Froese, Proc. Cambridge Phil. Soc. **53**, 206 (1957).

[17] It may be noted that the new term is by no means small in view of high accuracy available, e.g., isomer shift of W with respect to Fe is 0.0151±0.0002 cm/sec as given by J. W. Burton, H. Frauenfelder, and R. P. Goswin, in *Applications of the Mössbauer Effect* (International Atomic Energy Agency, Vienna, 1966), p. 73.