PHYSICAL REVIEW B VOLUME 9, NUMBER 11 1 JUNE 1974

Contribution of two-phonon processes to the spin-lattice relaxation rate of Kramers ions*

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(Received 21 December 1973)

We consider the contribution of two-phonon processes to the spin-lattice relaxation rate of Kramers ions. In particular, we study the interference between nonresonant and resonant processes when the lowest excited doublet lies well below the Debye limit. In this case, to a good approximation, the relaxation rate is the sum of a term proportional to $(e^{\Delta/kT}-1)^{-1}$ and a more complex term which at low temperatures is proportional to T^9. We also consider the case of the lowest excited doublet above the Debye limit.

I. INTRODUCTION

In this paper, we shall study the contribution of two-phonon processes to the spin-lattice relaxation rate of Kramers ions and concentrate on the interference between nonresonant and resonant processes when the lowest excited doublet lies well below the Debye limit.

To first order in the phonon operators, the interaction between the orbital motion of the electrons of a paramagnetic ion and the surrounding ions may be expressed as[1]

$$\mathcal{H}_{\mathrm{OL}}=\sum_{\substack{i,m\\ l=2,4,\ldots}} V(\Gamma_{ig},\, l)\, C(\Gamma_{ig},\, l,\, m)\,\epsilon(\Gamma_{ig},\, m),$$

where $C(\Gamma_{ig},\, l,\, m)$ are linear combinations of the operator equivalents O_l^q which transform as the mth subvector of the representation Γ_{ig}, $V(\Gamma_{ig},\, l)$ are coefficients independent of m, and $\epsilon(\Gamma_{ig},\, m)$ are linear combinations of the strain tensor which transform as the mth subvector of the Γ_{ig} representation and may be written[2,3]

$$\epsilon(\Gamma_{ig},\, m)=\sum_{\vec{k},s} i\left(\frac{\hbar}{2M\omega_{\vec{k}s}}\right)^{1/2}(b_{\vec{k}s}-b_{\vec{k}s}^{\dagger})R_{\vec{k}s}(\Gamma_{ig},\, m)\,.$$

Here M is the mass of the whole crystal, $\omega_{\vec{k}s}$ is the frequency of a phonon of wave vector $\vec{k}$ and polarization s, $b_{\vec{k}s}$ and $b_{\vec{k}s}^{\dagger}$ are phonon destruction and creation operators, and $R_{\vec{k}s}(\Gamma_{ig},\, m)$ are coefficients (some of which are listed by Orbach and Stapleton[3]) which in the long-wavelength limit become equal to $|\vec{k}|R_{\hat{k}s}(\Gamma_{ig},\, m)$, where $R_{\hat{k}s}(\Gamma_{ig},\, m)$ is independent of the size of $\vec{k}$.

We will not concern ourselves with second-order terms in phonon operators because, for Kramers ions, neglecting the effects of the Zeeman interaction, such terms have zero matrix elements between the components of one doublet.

Derivations of the relaxation rate for two-phonon processes can be found in the literature[3–5] and will not be reproduced here.

When there is only one excited doublet c, d at an energy Δ above the ground doublet a, b, in the long wavelength limit, assuming a Debye model for the phonon spectrum, we have

$$\frac{1}{T_1}=\frac{1}{(2\pi)^5}\,\frac{1}{2\rho^2}\Bigg(\sum_{s,s'}\frac{1}{v_s^5 v_{s'}^5}\int\!\!\int d\Omega_k\, d\Omega_{k'}\Bigg|\sum_{\substack{i,l,m\\ i',l',m'}} V(\Gamma_{ig},\, l)V(\Gamma_{i'g},\, l')\langle b|C(\Gamma_{ig},\, l,\, m)|c\rangle\langle c|C(\Gamma_{i'g},\, l',\, m')|a\rangle$$
$$\times[R_{\hat{k}s}(\Gamma_{ig},\, m)R_{\hat{k}'s'}(\Gamma_{i'g},\, m')-R_{\hat{k}s}(\Gamma_{i'g},\, m')R_{\hat{k}'s'}(\Gamma_{ig},\, m)]\Bigg|^2\Bigg)$$
$$\times\int_0^{\omega_{\max}}\omega^6\, d\omega\, n(\omega)[n(\omega)+1]\left|\frac{1}{\Delta-\hbar\omega-\frac{1}{2}i\Gamma}-\frac{1}{\Delta+\hbar\omega-\frac{1}{2}i\Gamma}\right|^2,$$

where $n(\omega)=(e^{\hbar\omega/kT}-1)^{-1}$, ρ is the density of the crystal, v_s and $v_{s'}$ represent the velocity of phonons of polarization s and s', Γ is the width of each component of the excited doublet involved in the relaxation and the integration over $d\Omega_k d\Omega_{k'}$ is a double angular integration in k space.

After the following change of variables

$$x=\hbar\omega/\Delta\,,\quad \gamma=\Gamma/2\Delta\,,$$

the integral I over ω can be rewritten

$$I=\frac{\Delta^5}{\hbar^7}\int_0^{k\Theta_D/\Delta}\frac{x^8}{\sinh^2(x\Delta/2kT)}\times\frac{dx}{[(1+x)^2+\gamma^2][(1-x)^2+\gamma^2]}\,. \tag{1}$$

Stoneham[6] and more recently Lyo[5] have studied similar integrals.

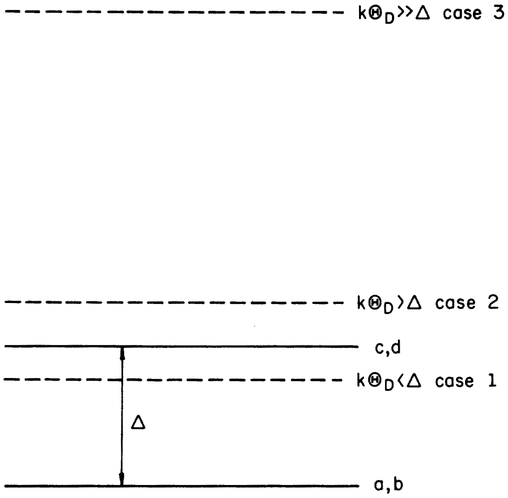

FIG. 1. Energy-level diagram showing the three different cases studied.

II. NONRESONANT RAMAN PROCESS

When the excited doublet is above the Debye limit (Fig. 1, case 1), expanding $([(1+x)^2+\gamma^2][(1-x)^2+\gamma^2])^{-1}$ in powers of x, the above integral can be rewritten[7]

$$I=\frac{4k^9T^9}{\hbar^7\Delta^4}\sum_{n=0}^{\infty}\frac{1}{r^{2n+4}}\frac{\sin(2n+2)\theta}{\sin 2\theta}\left(\frac{kT}{\Delta}\right)^{2n}J_{8+2n}(\Theta_D/T)\ ,$$

where

$$r=(1+\gamma^2)^{1/2}\ ,$$

$$\theta=\sin^{-1}[\gamma/(1+\gamma^2)^{1/2}]\ ,$$

$$J_q(x)=\int_0^x\frac{t^qe^t}{(e^t-1)^2}\,dt\ .$$

More explicitly, letting $v_s=v_{s'}=v$, we find

$$\frac{1}{T_1}\propto\frac{\hbar^2k^9}{\rho^2v^{10}\Delta^4}\left(\frac{T}{\hbar}\right)^9\frac{J_8(\Theta_D/T)}{(1+\gamma^2)^2}$$
$$\times\left[1+2\frac{1-\gamma^2}{(1+\gamma^2)^2}\left(\frac{kT}{\Delta}\right)^2\frac{J_{10}(\Theta_D/T)}{J_8(\Theta_D/T)}+\frac{3-10\gamma^2+3\gamma^4}{(1+\gamma^2)^4}\left(\frac{kT}{\Delta}\right)^4\frac{J_{12}(\Theta_D/T)}{J_8(\Theta_D/T)}+\cdots\right].$$

This reduces to the well-known T^9 Raman result at low temperatures. Only if the excited doublet is well above the Debye limit is the temperature dependence of the relaxation rate described by the "usual" $T^9J_8(\Theta_D/T)$. If this condition is not met, the temperature dependence of the Raman process may be described locally by T^n,[8] where n first goes from 9 to a maximum and then decreases to 2 in the high-temperature limit. This corresponds to the fact that more terms are needed in the series expansion in order to approximate the integral.

Also, one may notice the weak dependence of the Raman rate on the width of the components of the excited doublet, provided that this doublet is not too close to the Debye limit. Figure 2(a) shows the dependence of the integral in Eq. (1) on tempera-

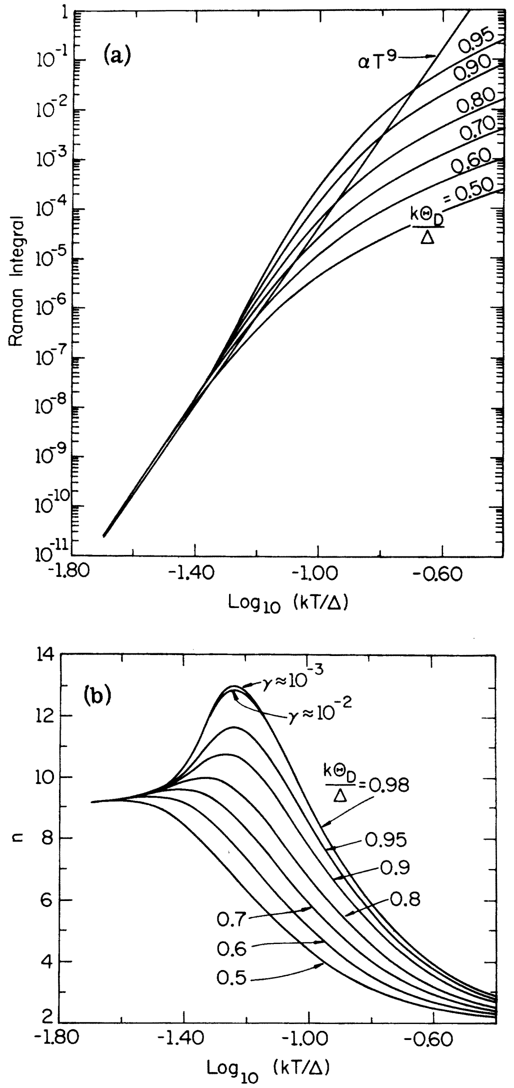

FIG. 2. (a) Temperature dependence of the integral in Eq. (1) when the excited doublet lies above the Debye limit (Fig. 1, case 1), for various values of the parameter $k\Theta_D/\Delta$. In the temperature range studied, changes of the reduced width γ of the excited doublet, provided it is kept below 10^{-2}, do not produce visible changes in the figure. The function $4(kT/\Delta)^9J_8(\infty)$, where J_8 is the transport integral defined in the text, is also plotted for comparison. (b) Temperature dependence of the exponent of T^n (locally determined) for various values of the parameter $k\Theta_D/\Delta$. As the excited doublet gets closer to the Debye limit, a small dependence of the relaxation rate upon the reduced width γ of the excited doublet appears and is displayed for $k\Theta_D/\Delta=0.98$.

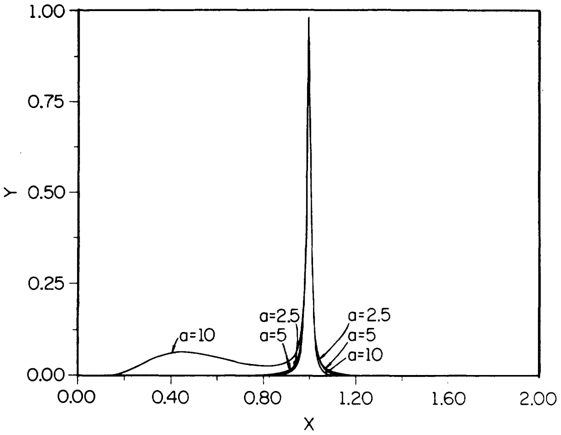

FIG. 3. Integrand y of Eq. (1) properly scaled (see text) for various values of the parameter a.

ture, Δ and Θ_D. In Fig. 2(b), the dependence of n upon the same parameters is given, and the extra dependence on γ which appears when the doublet approaches the Debye limit is also shown.

III. RESONANT RAMAN PROCESS

When the excited doublet is below the Debye limit, the situation is much more complex. For convenience in doing the algebra, let $a=\Delta/2kT$. Figure 3 shows the x dependence of the integrand of Eq. (1) multiplied by the scaling factor $4\gamma^2(a)\sinh^2 a$, for various values of a (this scaling factor is used only to allow the display of many curves on the same graph and has no immediate physical meaning); we have written the temperature-dependent reduced width of each component of the excited doublet

$$\gamma=\gamma_0 e^{2a}/(e^{2a}-1) \text{ with } \gamma_0=\mathfrak{M}\Delta^2/v^5\rho\hbar^3,$$

where $\mathfrak{M}$ is a quantity involving matrix elements of the crystal-field Hamiltonian given in detail by Orbach[4] and γ_0 is known to be, usually, on the order of 10^{-2} or lower from the experimentally determined coefficient of the resonant Raman process and was taken equal to 10^{-2} for Fig. 3.

If $k\Theta_D/\Delta > 1.25$, then to a good approximation it can be seen from Fig. 3 that the upper limit of the integral in Eq. (1) can be taken to be infinity for temperatures lower than $\Delta/5k$, and the larger $k\Theta_D/\Delta$ happens to be, the higher the temperature at which this approximation breaks down.

Using the results given in the Appendix and expanding in powers of γ, we find

$$\frac{1}{T_1}\propto\frac{\Delta^5}{4\rho^2v^{10}\hbar^7}\left[\frac{4\pi/\gamma_0}{e^{2a}-1}+\frac{2}{15}\frac{\pi^4}{a^5}+\frac{4\pi^2}{3a^3}\right.$$
$$\left.-\frac{12}{a}+\frac{14}{\pi}\operatorname{Im}\psi'\left(-\frac{ia}{\pi}\right)-\frac{2a}{\pi^2}\operatorname{Re}\psi''\left(-\frac{ia}{\pi}\right)+O(\gamma_0)\right], \qquad (2)$$

where $O(\gamma_0)$ represents terms of order 1 and higher in γ_0, which we will discuss later, and where we have used the equality

$$\operatorname{Re}\psi'(iy)=-\frac{1}{2y^2}-\frac{\pi^2}{2}\frac{1}{\sinh^2\pi y},$$

ψ' and ψ'' being the well known trigamma and tetragamma functions.[9] This expression has the following asymptotic expansion when a tends to infinity (T goes to zero):

$$\frac{1}{T_1}\propto\frac{\Delta^5}{\rho^2v^{10}\hbar^7}\left[\frac{\pi/\gamma_0}{e^{2a}-1}+\sum_{j=4}^{\infty}(-1)^j\right.$$
$$\left.\times\frac{\pi^{2j}}{a^{2j+1}}B_{2j}(3-j)+O(\gamma_0)\right],$$

where we have used Abramowitz and Stegun's[9] convention for the Bernoulli numbers. It is remarkable that, in spite of the apparent complexity of the problem, there is no power of T lower than 9. Explicitly, the first few terms read

$$\frac{1}{T_1}\propto\frac{\Delta^5}{\rho^2v^{10}\hbar^7}\left[\frac{\pi}{\gamma_0}\frac{1}{e^{\Delta/kT}-1}+\frac{256\pi^8k^9T^9}{15\Delta^9}\right.$$
$$\left.+\frac{10240\pi^{10}k^{11}T^{11}}{33\Delta^{11}}+\cdots+O(\gamma_0)\right].$$

The first term within the brackets is the usual resonant Raman term, the next one is the nonresonant T^9 Raman term, and the sum of the following

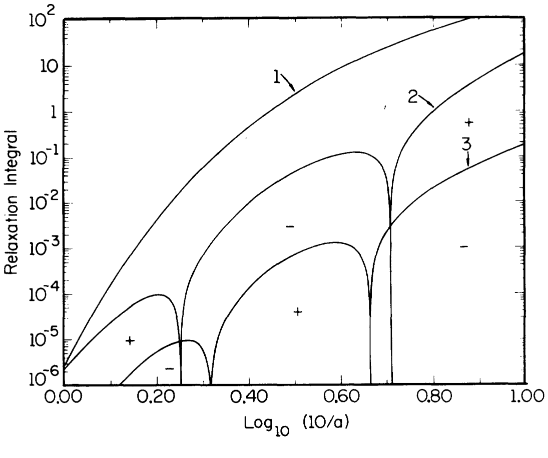

FIG. 4. Plot of the three leading terms in the relaxation integral when the excited doublet is below the Debye limit (Fig. 1, case 2). Curve number 1 is the term in $1/\gamma_0$ within the square brackets of Eq. (2), curve number 2 is the absolute value of the term in $(\gamma_0)^0$ within the square brackets in Eq. (2), and curve number 3 is the absolute value of the term in γ_0 given in Eq. (3). The signs of the terms in $(\gamma_0)^0$ and γ_0 are indicated on the figure. The curves were computed with $\gamma_0=10^{-2}$.

terms is the low-temperature asymptotic expansion of the interference between resonant and nonresonant processes.

As shown by direct computer calculation, the asymptotic expansion for the trigamma and tetragamma functions becomes useless around $T=\Delta/15k$. In fact, the coefficient of the term in $(\gamma_0)^0$ in Eq. (2), which is positive as expected at low temperatures, vanishes around $T=\Delta/11.24k$ and remains negative until $T=\Delta/3.90k$, after which it becomes positive again. The rapid change of this coefficient over two rather narrow temperature ranges (see Figs. 4 and 5) should be difficult to observe because it produces only (and roughly) $100\gamma_0\%$ change to the total relaxation unless, of course, there are systems for which γ_0 is larger.

Since at very low temperatures the term in $(\gamma_0)^0$ becomes larger than that in $(\gamma_0)^{-1}$ [i.e., the relaxation rate varies as T^9 instead of $(e^{\Delta/kT}-1)^{-1}$ at higher temperatures], one may wonder whether such a behavior is to be expected from the next term, in γ_0. Still expanding the results derived in the Appendix, we find

$$O(\gamma_0)=\gamma_0\frac{e^a}{2}\left(14a\pi\frac{\cosh a}{\sinh^4 a}-\frac{21\pi}{\sinh^3 a}\right.$$

$$\left.-\frac{2a^2\pi}{\sinh^3 a}-\frac{3a^2\pi}{\sinh^5 a}\right)+O(\gamma_0^2), \qquad (3)$$

where $O(\gamma_0^2)$ represents terms of order 2 and higher in γ_0. At most, the term in γ_0 is (see Figs. 4 and 5) $10\gamma_0$ times the term in $(\gamma_0)^0$ and, for usual values of γ_0 it can be neglected, its biggest effects being to slightly shift the two zeros of the nonresonant term.

Therefore, for values of γ_0 smaller than 10^{-2}, Eq. (2) is a good approximation of the relaxation integral over a temperature range determined by the position of the excited state with respect to the Debye limit, as briefly discussed earlier.

If $k\Theta_D/\Delta$ is large (Fig. 1, case 3), Eq. (1) can be approximated by Eq. (2) even for small values of a; then, the high-temperature relaxation rate is given by

$$1/T_1 \propto T^5,$$

the well-known result for systems having a low-lying excited state.[10]

IV. CONCLUSION

We have studied the two-phonon relaxation processes for Kramers systems for which the lowest excited doublet is far removed from the others, with the assumption that the phonon spectrum follows a Debye model. When the lowest doublet is below the Debye limit, we showed that, to a good approximation, the relaxation rate is the sum of a term proportional to $(e^{\Delta/kT}-1)^{-1}$ (the resonant Raman term) and a somewhat more complicated term which, at low temperatures, is proportional to T^9 (the nonresonant Raman term).

ACKNOWLEDGMENT

The author wishes to express his gratitude to Professor Harvey J. Stapleton for stimulating discussions on the theory of spin-lattice relaxation and for reading the manuscript and suggesting ways to improve it.

APPENDIX

In this appendix, we will evaluate the following integral:

$$J=\int_0^\infty \frac{x^8}{\sinh^2 ax}\frac{dx}{[(1+x)^2+\gamma^2][(1-x)^2+\gamma^2]}, \quad a=\frac{\Delta}{2kT}.$$

Making use of the equality

$$\frac{1}{[(1+x)^2+\gamma^2][(1-x)^2+\gamma^2]}$$

$$=\frac{1}{4x}\left[\frac{1}{(1-x)^2+\gamma^2}-\frac{1}{(1+x)^2+\gamma^2}\right],$$

we obtain

$$J=\frac{1}{4}\int_{-\infty}^{+\infty}\frac{x^7}{\sinh^2 ax}\frac{dx}{(1-x)^2+\gamma^2}.$$

We also have

$$\frac{1}{(1-x)^2+\gamma^2}=\frac{1}{\gamma}\int_0^\infty e^{-\gamma y}\cos[(1-x)y]\,dy,$$

which yields

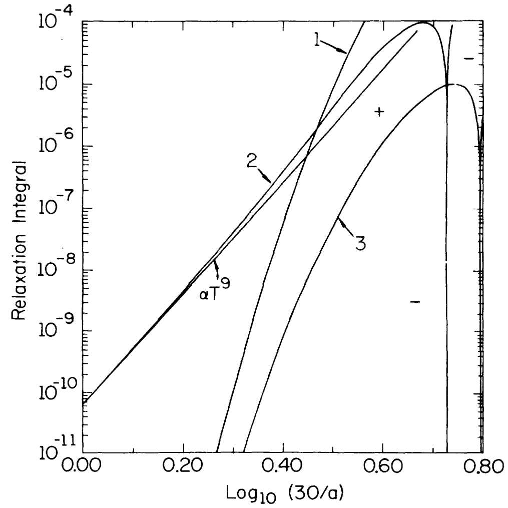

FIG. 5. The same terms as in Fig. 4 are plotted at lower temperatures and the curve $1024\pi^8(kT)^9/(15\,\Delta^9)$ is also plotted to display the low-temperature behavior of the relaxation. The same value of γ_0 was used as in Fig. 4.

$$J=\frac{1}{4\gamma}\int_0^\infty e^{-\gamma y}\sin y\,dy\int_{-\infty}^{+\infty}\frac{x^7\sin xy}{\sinh^2 ax}\,dx\,,$$

or, equivalently,

$$J=-\frac{1}{4\gamma}\int_0^\infty e^{-\gamma y}\sin y\,\frac{d^7}{dy^7}\left(\int_{-\infty}^{+\infty}\frac{1-\cos xy}{\sinh^2 ax}\,dx\right)dy\,.$$

Fortunately, the innermost integral can be expressed in terms of simple functions^{11}:

$$\int_{-\infty}^{+\infty}\frac{1-\cos xy}{\sinh^2 ax}\,dx=4\int_0^\infty\frac{\sin^2(xy/2)\,dx}{\sinh^2 ax}$$

$$=\frac{2}{a}\,\frac{\pi y/a}{e^{\pi y/a}-1}+\frac{\pi y}{a^2}-\frac{2}{a}\,.$$

After integrating by parts, the given integral can be written

$$J=\frac{1}{30}\,\frac{\pi^4}{a^5}+(1-\gamma^2)\,\frac{\pi^2}{3a^3}+\frac{1}{4\gamma}\int_0^\infty\left[\frac{d^7}{dy^7}\,(e^{-\gamma y}\sin y)\right]$$

$$\times\left(\frac{2\pi}{a^2}\,\frac{y}{e^{\pi y/a}-1}+\frac{\pi y}{a^2}-\frac{2}{a}\right)dy\,.$$

It can easily be seen that

$$\frac{d^7}{dy^7}\,(e^{-\gamma y}\sin y)=(-1+21\gamma^2-35\gamma^4+7\gamma^6)\cos y\,e^{-\gamma y}$$

$$+\gamma(7-35\gamma^2+21\gamma^4-\gamma^6)\sin y\,e^{-\gamma y}\,.$$

Therefore, all that is to be computed are integrals of the form

$$\int_0^\infty\frac{ye^{-\gamma y}\,{}^{\sin}_{\cos}\,y\,dy}{e^{\pi y/a}-1},\quad\int_0^\infty ye^{-\gamma y}\,{}^{\sin}_{\cos}\,y\,dy,\quad\int_0^\infty e^{-\gamma y}\,{}^{\sin}_{\cos}\,y\,dy\,.$$

The last two of these integrals are trivial; the first one is

$$\frac{a^2}{\pi^2}\,{}^{\mathrm{Im}}_{\mathrm{Re}}\,[\psi'(1+(\gamma-i)a/\pi)]$$

where $\psi'(z)$ is the trigamma function.[9] The final result is then

$$J=\frac{\pi^4}{30a^5}+(1-\gamma^2)\,\frac{\pi^2}{3a^3}+\frac{1}{4\gamma}(-1+21\gamma^2-35\gamma^4+7\gamma^6)$$

$$\times\left[\frac{2}{\pi}\mathrm{Re}\psi'((\gamma-i)a/\pi)+\frac{\pi}{a^2}\,\frac{1-\gamma^2}{(1+\gamma^2)^2}-\frac{2\gamma}{a(1+\gamma^2)}\right]$$

$$+\tfrac{1}{4}(7-35\gamma^2+21\gamma^4-\gamma^6)\left[\frac{2}{\pi}\mathrm{Im}\psi'((\gamma-i)a/\pi)\right.$$

$$\left.-\frac{2\pi}{a^2}\,\frac{\gamma}{(1+\gamma^2)^2}-\frac{2}{a}\,\frac{1}{1+\gamma^2}\right]\,.$$

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*This research was supported in part by the National Science Foundation under Grant No. GH 33634.

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[9] There are a few current notations for the polygamma functions. We used that of M. Abramowitz and I. Stegun, *Handbook of Mathematical Functions* (U. S. Natl. Bur. Stand., Washington, D. C., 1964), i.e., $\psi^{(n)}(z)=d^{n+1}\ln\Gamma(z)/dz^{n+1}$, where $\Gamma(z)$ is the gamma function. Short tables of $\mathrm{Im}\psi'(ix)$ and $\mathrm{Re}\psi''(ix)$ are available from us upon request.

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[11] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products* (Academic, New York, 1965), formula number 3.9864; one way to derive this formula is to expand $\sin^2(xy/2)$ in series, the result being that given above, except valid only for $y<2a$; then, use analytic continuation and show that the result is valid for all real y.