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Paramagnetic Relaxation and the Equilibrium of Lattice Oscillators

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The present paper is rather negative in character. Its aim is to show that the conventional models of paramagnetic relaxation cannot be used at helium temperatures, because the lattice vibrations cannot possibly serve as a thermostat in the way ordinarily supposed. Namely, if the quanta exchanged between the spin system and the lattice oscillators are of the order 0.2 cm^{-1} characteristic of the usual Stark splittings in chrome or iron alum, the spins will be in thermal contact only with oscillators at the extreme low frequency end of the lattice spectrum which are too few in number to conduct away the surplus spin energy. It is found that this limited band of oscillators is interrupted much more frequently by interactions with the spins than by (a) collisions with the walls or (b) interplay with other oscillators due to anharmonic terms (calculated in the next paper). Consequently the lattice vibrations in thermal contact with the spin system will be at nearly the spin temperature, and not at that of the helium container as ordinarily supposed. Impurities with abnormally large Stark splittings, of the order 2.0 cm^{-1}, would make a wider band of lattice oscillators available and so would avoid the difficulty of insufficient lattice conductivity, but it is very doubtful whether the impurities could be in thermal equilibrium with the great bulk of the paramagnetic ions. By thus showing that conventional hypotheses will not work, we aim to pave the way for a future paper proposing a rather unusual substitute conduction mechanism which is, however, compatible with the thermodynamic formulae of Casimir and du Pré.

Introduction.—In a previous paper[1] the writer computed paramagnetic relaxation times for chromium and titanium alum on the basis of the thermodynamical model of Casimir and du Pré,[2] wherein the lattice oscillators are treated as a thermostat as far as the interchange of energy with the spins is concerned. These calculations were in fairly satisfactory agreement with experiment at liquid-air temperatures, but failed completely at helium temperatures, giving here a wrong order of magnitude for titanium alum, and the wrong sign for the dependence of the relaxation time of chrome alum on the strength of the applied magnetic field. It is the purpose of the present article to point out that it is impossible for the lattice oscillators to preserve a constant temperature in the face of frequent energy transfers with the spin. Hence it is not surprising that the calculations based on the ordinary assumptions should partially fail and so, apart from basic thermodynamic features, the conventional theory must somehow be modified. It was emphasized by Casimir himself[3] that at low temperatures the lattice, inclusive of all oscillators, has such a small heat capacity that it can serve as a thermostat only if it is surrounded by a bath of liquid helium, and is in equilibrium with the latter. However, the situation is much more acute even than this, because of the fact that the work required to turn over a spin against either the applied magnetic or the crystalline field is very small, not more than 0.2 cm^{-1}, for example, in chrome or iron alum. Hence the conservation of energy allows exchange of energy only between the spins and oscillators of very low frequency ω, which are far from numerous inasmuch as the density of oscillators is proportional to ω^2 and which consequently cannot conduct energy rapidly to the walls. The same difficulty does not arise in connection with the calculations at liquid-air temperatures, as here interaction between spin and lattice is secured by means of second-order processes wherein a spin scatters a lattice quantum of comparatively high energy with only a relatively small modulation of frequency, like the Raman mechanism in radiation theory. Such processes, however, have been shown by Waller[4] and others to be of minor importance at very low temperatures.

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[1] J. H. Van Vleck, Phys. Rev. **57**, 426, 1052 (1940).

[2] H. B. G. Casimir and F. K. du Pré, Physica **5**, 507 (1938).

[3] H. B. G. Casimir, Physica **6**, 156 (1939).

[4] I. Waller, Zeits. f. Physik **79**, 370 (1932).

Width of the low frequency band.—If the spin of a paramagnetic atom had sharply defined energy levels, split only by a definite crystalline field and the applied magnetic field, then because of the conservation of energy the possible energy exchanges between spin and lattice would form a discrete spectrum, and only an infinitesimal fraction of the lattice oscillators would be on "speaking terms" with the spin. Actually, the energy-exchange spectrum will be blurred into a continuum for two reasons. In the first place, the spin-spin interaction will introduce a fluctuating effective magnetic field acting upon the atom, which is superposed upon the applied field, and which has a continuous distribution of magnitudes. Secondly, there is a diffuseness in energy levels due to the uncertainty principle, because the harmonic oscillations do not persist over a large number of periods.

For purposes of estimating the order of magnitude of the spreading in energy due to spin-spin interaction, it will suffice to assume that the latter broadens the spin levels into bands of width $2K\beta/h$ where β is the Bohr magneton number, and K is the root mean square spin-spin field. The frequency distribution law for the oscillators is $C\omega^2 d\omega$, and their total number is $\frac{1}{3}C(k\theta/h)^3$ where C is a constant and $k\theta/h$ is the usual Debye cut-off frequency. Hence the fraction x of the total number of oscillators which is in thermal contact with the spins becomes $x \sim 2\beta K \cdot h^2\omega^2/\frac{1}{3}k^3\theta^3$. Here $h\omega$, the center of the energy band of allowed exchanges, is of the order 0.2 cm^{-1} in chrome alum, the precise value naturally depending on the strength of the applied magnetic field, while $k\theta/h$ is approximately 230 cm^{-1}, and we previously[1] estimated $K=290$ gauss, so that $\beta K \sim 10^{-2}$ cm^{-1}. Thus only about one in 10^{10} of the total number of lattice oscillators is on "speaking terms" with the spin system. The observed relaxation time τ for a spin is about 10^{-2} sec. for chrome or iron alum. The number of exchanges or interruptions per second for an oscillator accessible to the spin is $\nu_i = (1/3x\tau y)$ where y is the total number of atoms per paramagnetic atom ($=48$ in $\text{KCr(SO}_4)_2 \cdot 12\text{H}_2\text{O}$). This interruption frequency ν_i is thus of the order 10^{10} sec.^{-1}.

The estimates of the preceding paragraph, however, overlook the fact that according to the uncertainty principle, or its equivalent, one is justified in talking of the proper frequency ω of a lattice vibration only if it persists uninterrupted over several periods. Our preceding estimate of ν_i is about 10 times as large as ω. Consequently there will be a diffuseness in the oscillator levels. The corresponding blurring of spin states is negligible, as the spin-lattice energy exchanges are prorated among the spins of all paramagnetic atoms, much more numerous than the limited number of low frequency oscillators. This diffuseness makes the spins capable of exchanging energy with more oscillators than otherwise. The effect is roughly the same as though one permitted transitions in which conservation of energy based upon ideal monochromatic vibrations failed by amounts up to $h\nu_i$. Consequently we should at first sight expect the width of the zone of oscillators accessible to the spin to be of the order 10^{10} sec.^{-1} or 1 cm^{-1}, as this was our estimate of ν_i in the preceding paragraph. However, we must allow for the fact that when the burden of spin exchanges is distributed over a wider band of oscillators, the interruption frequency per oscillator is diminished, and so we ought to use a smaller value of ν_i as soon as the band width becomes greater than that 10^{-2} cm^{-1} used to obtain our estimate 10^{10} sec.^{-1}. Consequently, when allowance is made for this compensating effect, the value of ν_i is changed to 10^9 sec.^{-1}, and the correspoindng zone-width to 0.1 cm^{-1}. This estimate may seem to be somewhat high because line breadth tends in general to be rather less than the interruption frequency, but we may regard this tendency as roughly counterbalanced by the fact that there are really several frequency bands, instead of one as we assume. Namely, in the alums there are four paramagnetic ions in the unit cell, and as a result there are four orientations of the applied magnetic field relative to the microscopic trigonal field, and hence four patterns for the decomposition of the energy levels; furthermore even one ion may have more than one frequency interval, as its ground state is usually split into more than two components even without spin-spin interaction or blurring due to the uncertainty principle.

The mechanisms (a) and (b).—From the above discussion, it appears that the oscillators which can exchange energy with the spin system are confined to a zone of width about 0.1 cm^{-1}. However, if no more oscillators than this are on "speaking terms" with the spin, they will be unable to transfer energy fast enough between the spin system and the helium bath to account for paramagnetic relaxation times as short as those observed experimentally. Fröhlich and Heitler[5] have shown that the heat conductivity of the spin system itself is negligible. Hence the heat flow between the spin system and the boundary must take place via the lattice oscillators. Two possible mechanisms for this flow are, (a) *direct coupling between the low frequency oscillators and the helium bath* and, (b) *interaction of the low frequency oscillators with those of higher frequency, through anharmonic terms.* In (b) there must be indirect contact between our low frequency oscillators and the bath via ordinary oscillators of higher frequency, for we have already noted that the heat capacity of the entire lattice system is inadequate for it to serve as a thermostat unless it is in equilibrium with the bath. We call vibrations of the "low frequency" type if their quanta are commensurate with the energy required to turn over a spin, and if they can thus exchange energy with the spin system. By the term "ordinary oscillators" we mean those whose frequencies do not appreciably exceed kT/h, as vibrations with $\omega \gg kT/h$ are not appreciably excited, because of the Boltzmann factor, and so need not be considered. A spin quantum is about one-tenth of kT, in the helium region, and so the low frequency oscillators are much less abundant than the ordinary ones.

Inadequate conductivity of the low frequency oscillators.—To examine whether the mechanism (a) can be effective, that is to say, whether the temperature T_L of the low frequency oscillators can be equilibrated by direct contact with the surrounding helium bath of temperature T_0, we imagine that we have a spherical specimen of radius R and suppose that the elastic waves are uninterrupted except when they interact with a spin or reach the walls, as this is the extreme case most favorable for the penetration of the bath temperature into the specimen. As already emphasized by Casimir in another connection,[6] the mathematical analysis appropriate to this model corresponds essentially to radiation theory rather than to ordinary conduction. We may thus consider that we have a spherical *hohlraum* such that the elastic waves impinging on the wall have a temperature T_L, whereas those emitted by the walls have a temperature T_0. If $u(T)$ is the energy per unit volume of oscillators at temperature T, then the analogue of radiation intensity is $I(T)=vu(T)/4\pi$, where v is the velocity of sound (2.3×10^5 cm/sec. in the alums). Unit wall area absorbs energy $\int\int I(T_L)\cos\theta d\Omega=\frac{1}{4}vu(T_L)$ per unit time, and correspondingly emits $\frac{1}{4}vu(T_0)$. If T_L-T_0 is small, we may replace $u(T_L)-u(T_0)$ by $c(T_L-T_0)f(\omega)\Delta\omega$, where $f(\omega)\Delta\omega$ is the number of low frequency oscillators per unit volume in the interval $\Delta\omega$, and c is the mean specific heat per oscillator. Hence the rate at which heat is transferred from the low frequency oscillators to the helium bath is

$$dQ/dT=a(T_L-T_0),\quad \text{with}\quad a=\pi R^2 vcf(\omega)\Delta\omega. \qquad (1)$$

We can take c to have the classical value $k=1.37\times 10^{-16}$ ergs/deg. since our low frequency oscillators have quanta small compared to kT. We may suppose $f(\omega)\cdot\Delta\omega$ to be of the order 3.4×10^{14}, since the formula for the number of oscillators per unit volume in the frequency interval ω, $\omega+\Delta\omega$ is $12\pi v^{-3}\omega^2\Delta\omega$ and since our low frequency band involves an ω and $\Delta\omega$ about 6×10^9 and 3×10^9 sec.^{-1}, respectively. The conductivity a is consequently $3.3\times 10^{-3}R^2$ watts/deg.

Now according to the thermodynamical theory of Casimir and du Pré,[2] the rate at which heat flows from the spin system to the low frequency oscillators is

$$dQ/dt=\alpha(T_S-T_L),\quad \text{with}\quad \alpha=(4\pi R^3/3)c_S/\tau. \qquad (2)$$

Here T_S and c_S are, respectively, the spin temperature and the spin specific heat per unit volume, and τ is the paramagnetic relaxation time. The numerical value of c_S is $4800T^{-2}$ ergs/cc, while τ is the order 10^{-2} in the helium region. Consequently at 1.4°K, the conductivity constant α involved in (2) is about $10^{-1}R^3$ watts/deg. Since the heat capacity of the low frequency oscillators is negligible compared to that of the spin system, the heat flows (1) and (2) must be equal, whence $(T_L-T_0)/(T_S-T_L)=\alpha/a$. Clearly, if these oscillators are to serve as a

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[5] H. Fröhlich and W. Heitler, Proc. Roy. Soc. **A155**, 640 (1936).

[6] H. B. G. Casimir, Physica **5**, 495 (1938).

thermostat, at substantially a temperature T_0, we must have this ratio small compared to unity. With our estimates of α and a, however, α is thirty times as large as a for a specimen 1 cm in radius, and is three times as great even if R is as small as 0.1 cm. In other words the low frequency oscillators are interrupted much less frequently by collisions with the walls than by spin impacts, and so have a temperature much closer to that of the spin system than of the bath.

The calculation of the effectiveness of process (b), i.e., energy exchange between the low frequency and ordinary oscillators is more difficult, and is given in the following paper. We may assume that the ordinary oscillators are at the bath temperature T_0, as this supposition gives the most favorable case, and is, as a matter of fact fully warranted, as the ordinary oscillators are good conductors because they are so numerous. The calculations of the following paper, especially its Eq. (21), show that then the rate at which heat is taken away from the low frequency oscillators due to the process (b) is

$$dQ/dt = b(T_L - T_0), \tag{3}$$

with $b = 3\times 10^{-5}R^3$ watts/deg. at 1.4°K if, as before, we assume that the band of low frequency oscillators has $\omega = 6\times 10^9$, $\Delta\omega = 3\times 10^9$ sec.$^{-1}$. For a specimen 1 cm in radius, the process (b) is hence much less important than (a), and is nothing like rapid enough to make the low frequency oscillators serve as a thermostat.

Since we have seen that neither process (a) nor (b) conducts heat fast enough to make the temperature of the low frequency oscillators simulate that of the container, one immediately wonders whether possibly the correct model is instead one in which the low frequency oscillators are more nearly at the spin temperature, and in which the "bottle neck" for the flow of heat between the spin system and the helium bath is located between the low frequency oscillators and the container, rather than between the spin and these oscillators, as ordinarily supposed. Such a proposal, however, encounters serious difficulties, and is, in our opinion, not tenable. In the first place, the computed relaxation times become entirely too long. The values calculated under the conventional assumption that the low frequency oscillators serve as a thermostat were of about the right order of magnitude for chrome or iron alum, and already too great for titanium alum. With the mechanism (b), for instance, the formula for τ becomes $c_S(\alpha+b)/\alpha b$ instead of c_S/α, where c_S is the spin specific heat, and α, b are the conductivity constants for spin-lattice coupling and process (b), respectively. The modified formula corresponds to the fact that the conductivity due to two resistances $1/\alpha$, $1/b$ in series is $\alpha b/(\alpha+b)$. With mechanism (a), there is no unique formula for the relaxation time, as heat will be conducted away more rapidly from spins at the edges of the specimen, than those at the center. As a result the expressions for the dispersion and absorption become complicated functions of frequency, corresponding to a distribution of relaxation times τ wherein τ increases with the depth of penetration into the sample. Such a behavior is probably not in agreement with experiment, as the observed dispersion curves agree fairly well with those computed under the assumption of a single relaxation time. Another difficulty with (a) is that the mean relaxation time would increase with the volume of the specimen, whereas no dependence on size is found experimentally.[7] These complications due to spatial inhomogeneity do not arise in connection with (b), as in (b) the ordinary oscillators serve as a thermostat throughout the volume. However, in (b) there is the further objection that the temperature dependence of τ is wrong. Namely, the observed values of τ are approximately proportional to T^{-2}, whereas the theoretical expression $c_S(\alpha+b)/\alpha b$ is proportional to T^{-6} if $\alpha \gg b$, inasmuch as[8] $c_S \sim T^{-2}$, and as Eq. (21) of the following paper shows that $b \sim T^4$.

We thus find that neither mechanism (a) nor (b) can account for the observed flow of heat between the spin system and the container, unless one assumes that somehow most of the thermal contact between the spin system and the lattice is made directly between spins and a substantial portion of the "ordinary oscillators," whose frequencies are comparable with kT/h. In other words, energy exchange between spin and lattice takes place primarily in virtue of the handing back and forth of quanta which are

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[7] W. J. de Haas and F. K. du Pré, Physica **5**, 501 (1938).

[8] H. B. G. Casimir, W. J. de Haas, and D. de Klerk, Physica **6**, 241 (1939).

considerably larger than those of the order 0.2 cm^{-1} which represent the prevalent Stark splittings. If the spin system makes thermal contact with a sufficiently large fraction of the ordinary oscillators, the conductivity of the portion of the lattice in communication with the spin will be sufficient to dispose of the heat liberated by the latter, and the "bottle-neck" will be between the spin and the lattice, rather than between the lattice and the bath. An idea of the fraction of oscillators required can be obtained by referring to Eq. (1).[9] We require a conductivity 300, or more, times that previously computed on the basis of a zone of low frequency oscillators of width 3×10^9 sec.$^{-1}$, and mean frequency 6×10^9 sec.$^{-1}$, as then for a specimen of radius 1 cm, the constant a in (1) will become about 10 times that α in (2). To obtain this increased conductivity, we must use in (1) a value of $f(\omega)\Delta\omega$ about 300 times larger than formerly. As the oscillator density $f(\omega)$ is proportional to ω^2, the requisite increase will be obtained if we assume, for instance, that $h\omega=2.0$ cm^{-1}, and that the band width $h\Delta\omega$ is at least of the order 0.3 cm^{-1}, or alternatively, that $h\omega$ and $h\Delta\omega$ are each about 1.0 cm^{-1}.

Unfortunately it appears impossible to find any reasonable mechanism which will provide for the appreciable exchange of such abnormally large quanta between the spin system and lattice. Temperley[10] has suggested that several spins turn over simultaneously, but in our opinion,[1] the probability of such a process is negligible. Another possibility is that we have grossly underestimated the blurring due to the uncertainty principle. As we intimated in a previous paper,[1] most of the difficulties would disappear if the line breadth due to the uncertainty principle were very large, of the order 3×10^{10} sec.$^{-1}$ ($=1$ cm^{-1}), about ten times as large as estimated in the first part of the present article. However, it is very difficult to see how this value could be so seriously in error, especially since estimates of line breadth based simply on the interruption frequency tend to be too high rather than too low. (For instance, the line breadth[11] of a harmonic oscillator due to radiation does not increase with the quantum number, although the amplitude and hence the transition probability does.) A blurring as wide as 1 cm^{-1}, would make the effective oscillator density at low frequencies practically independent of frequency, instead of being proportional to ω^2 as in the Debye law, and is doubtless contradicted by experimental evidence in other fields, such as specific heats.

Effect of impurities.—A possibility which must be more seriously considered as a mechanism for the transfer of large quanta is the potential presence of impurities. By an impurity, we mean any paramagnetic ion whose splitting is very much larger than the mean value yielded by specific heat data, in other words is of the order 2.0 cm^{-1} instead of 0.2 cm^{-1}. The impurity need not necessarily be chemical, and instead can be an ordinary atom with an unusual crystalline (or perhaps even exchange) potential due to lattice imperfections, or in an abnormal valence state. The possible importance of impurities has beem emphasized to the writer by Professor Casimir, who points out that two samples not differing ostensibly in chemical and crystalline structure sometimes yield relaxation times differing by a factor 2 or more. The first question which arises in this connection is whether it is possible to have impurities which are sufficiently rare as to be without appreciable influence on the specific heat, etc., but which are abnormally potent in spin-lattice coupling. This question can

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[9] It may be objected that Eq. (1) based on the radiation model, furnishes only an upper limit to the conductivity, and so does not tell us the necessary number of oscillators, as this model does not take into account the possibility of the mean free path of an oscillator being terminated except by collisions with the walls. However, one can also solve the heat conduction problem for a sphere with surface at temperature T_0 and containing a source of intensity $\tau^{-1}c_S(T_S-T_0)$ per unit volume (cf. Eq. (2)). The necessary conductivity can then be gauged by the requirement that the temperature at the center of the sphere be much closer to T_0 than to T_S. If one assumes that the conductivity per oscillator in the alums is about the same as that found experimentally by de Haas and Biermasz (Physica **2**, 673 and **5**, 619) for other crystals at helium temperatures, the estimate of the necessary number of oscillators thus obtained, though somewhat larger, does not prove to be greatly different from that supplied by the simple radiation model. We aim to determine only rough orders of magnitude, and so throughout the paper it is not worth while to distinguish between $\int\omega^2d\omega$ and $\omega^2\Delta\omega$, or in the present connection to allow for the fact that the specific heat c in (1) does not quite reach the equipartition value k when $h\omega$ is as high as 2.0 cm^{-1}.

[10] C. N. V. Temperley, Proc. Camb. Phil. Soc. **35**, 256 (1939).

[11] V. Weisskopf and E. Wigner, Zeits. f. Physik **63**, 54; **65**, 18 (1930).

in a certain sense be answered in the affirmative. Namely, the specific heat is proportional to only the square of the Stark splitting ν of the spin levels, whereas the spin-lattice coupling is under certain conditions[12] proportional to ν^6. Hence, at first sight, it seems that if, say, 1 ion in 10^6 has 10 times the normal Stark splitting, the spin-lattice conductivity might be appreciably affected by such an impurity. However, this is not really the case, as the fact has been overlooked that such large spin quanta as 2.0 cm^{-1} cannot possibly achieve a common temperature with the more prevalent, tenfold smaller, quanta characteristic of the spins of the great majority of the ions. The energy exchanges among spins must satisfy the conservation of energy, and so spin temperatures can be equilibrated only by processes in which the turning over of a large quantum is offset by the simultaneous turning over of about 10 small quanta, due to spin-spin interaction. Such a cooperative or clustering phenomenon can be regarded as in many respects a generalization of the Temperley mechanism, and has a negligible probability (of the order e^{-50} or so). One way of escaping this difficulty is to assume that the impurities have a large over-all Stark splitting ν, but that the splitting $\Delta\nu$ between certain sub-states, say a doublet, is comparable with the usual Stark intervals. Then the relative, but not the total population of the two doublet components conforms to the spin temperature. Because of this fact, the catalytic effect of the impurity is not as great as previously estimated, as it can be shown that an extra factor $(\Delta\nu/\nu)^2$ is thereby introduced. Thus if the impurities have about 10 times the usual splitting, our previous requirement of 1 in 10^6 would be changed to 1 in 10^4. Such an abundance for impurities is presumably so high as to be out of the question, but quite irrespective of this fact it is highly unlikely that they would have the right kind of Stark pattern, wherein there are small intervals of just the right size superposed on the large. The most likely possibility of this type would appear to be ions with an odd number of electrons having a degenerate or nearly degenerate orbital state. Then there would be a large total splitting, but small doublets due to the Kramers degeneracy which are decomposed only by the magnetic field. The only example of this situation in the iron group is, however, Co^{++} if the crystalline field is of the usual nearly cubic type. Ions with an even number of electrons might have certain sub-states which separate only in virtue of the applied magnetic field, or of small deviations of the crystalline field from the dominant symmetry, but the difficulty is that there would be no matrix components of the spin-spin interaction between the different sub-states, so that transitions between the latter would be impossible. For example, an ion with $S=1$ (e.g., V^{+++}) has no matrix elements of spin between the two degenerate levels $M_S=\pm 1$ in an axial field. Thus, all told, any impurity mechanism appears to be too highly artificial to be at all reasonable.

Conclusion.—We seem to be between Scylla and Charybdis. We have shown that if the quanta exchanged between spin and lattice are comparable with the prevalent Stark splittings of the spin system, the latter is on "speaking terms" with only a very limited number of lattice oscillators, which are located at the extreme low frequency end of the spectrum, and which conduct heat to the walls or to the rest of the oscillators far too slowly to serve as a thermostat as presupposed in the ordinary thermodynamic model. On the other hand, we have seen that any mechanism, such as impurities, which involves the transfer of larger quanta, and which so makes more oscillators accessible, is highly improbable. There is, however, one more possibility, which we believe is the way out, and which we will consider in a future paper. It is that the conduction of heat from the spin system to the helium bath takes place via *virtual* rather than *real* lattice states, i.e., via a sort of ghost wave. This process, though compatible with Casimir's thermodynamic postulates, seems at first sight rather strange, and so we have gone to some detail in the present article to exhaust the other, more conventional possibilities.

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[12] Eq. (53) of reference 1 shows that the conductivity obviously contains a factor ν^4 because the splittings $W_{\eta'}-W_{\eta''}$ in (53) are proportional to ν. In addition there may be an extra factor ν^2 because increased splittings are usually the result of closer upper states and so are usually accompanied by larger perturbing matrix elements $H^{(k)}(\eta';\eta'')$. This can be seen, for instance, from the fact that Eq. (49) of reference 1 and Eq. (14) of J. Chem. Phys. **7**, 71 (1939) involve denominators of similar structure.