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Relation Between Paramagnetic Absorption and Susceptibility

S. A. Altshuler; Zhurnal Eksperimental'noy i Teoreticheskoy Fiziki, Vol 20, No 11, pp 1047-1050; Moscow/Leningrad, 1950.

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RELATION BETWEEN PARAMAGNETIC ABSORPTION AND SUSCEPTIBILITY

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Submitted 3 Apr 1950

/Abstract by the Author/

General integral relations between high-frequency susceptibility χ [cgs] and the coefficient χ'' of absorption are established for the case where the curves of paramagnetic dispersion and absorption express the dependence of χ' and χ'' on the magnitude of the applied static field H. These relations allow us, knowing $\chi'(H)$, to find $\chi''(H)$ and vice-versa. They may also be used for calibration of experimental curves of dispersion and absorption. The relations are verified by the experimental curves obtained by various authors for several frequencies.

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/Main Text/

Experimental investigations of paramagnetic relaxation do not give in most cases the absolute values of high-frequency susceptibility χ' and the absorption coefficient χ''. Usually we obtain as a result of measurements absorption and dispersion curves whose ordinates are expressed in arbitrary relative units. This limits the possibility of comparing the results of various measurements and causes difficulties in testing the theoretical conclusions on experimental data.

In 1947 L. D. Landau suggested, in a chat, using Kramers' relations [1] for establishing the absolute values of χ' and χ''. These relations, as is known, establish a general connection between χ' and χ'', considered as functions of the frequency ν [cgs] applied to the variable field. In nearly all cases, unfortunately,

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experiments of paramagnetic relaxation are conducted under conditions which leave the dependence of high-frequency susceptibility χ' and absorption coefficient χ'' upon frequency ν unknown. Usually the dependence of χ' and χ'' on the magnitude of the applied static magnetic field H, disposed either parallel or perpendicular to the variable magnetic field, are measured.

We shall attempt in the present article to explain how Kramers' relations should be modified in the case where the dependence of dispersion and absorption on the magnitude of the applied static field is discussed. We shall begin our derivation from the general expression of complex paramagnetic susceptibility [2]:

$$\chi = \chi' - i\chi'' = B \sum_{n,k,i,j} \frac{|M_{ni,kj}|^2}{h\nu_{ni,kj}} \left[f(\nu_{ni,kj}, \nu) + f(-\nu_{ni,kj}, \nu) \right] e^{-E_{ni}/kT} \qquad (1)$$

Here $M_{ni,kj}$ is the matrix element of the component of the magnetic moment along the direction of the variable magnetic field, related to two stationary states ni and kj; E_{ni} and E_{kj} are the energies of the paramagnetic particle in these states; $h\nu_{ni,kj} = E_{ni} - E_{kj}$; $B = 1/\Sigma e^{-E_{ni}/kT}$. The function $f(\nu_{ni,kj}, \nu)$ is given by

$$f(\nu_{ni,kj}, \nu) = \left[1 - i\nu_{ni,kj}\tau_{ni,kj}\right] / \left[1 + i(\nu - \nu_{ni,kj})\tau_{ni,kj}\right]$$

where $1/\tau_{ni,kj}$ characterizes the width of the absorption line connected with the transition $ni \leftrightarrow kj$.

The quanta numbers n and k indicate groups of energy levels, the intervals between which are comparable and higher than kT. The indices i and j indicate energy levels within each group, separated from each other by intervals small in comparison with kT. Usually a variable magnetic field is produced by a radio-wave oscillator; hence, if $n \neq k$, then $\nu \ll \nu_{ni,kj}$ and therefore we may assume $f(\nu_{ni,kj}, \nu) = 1$. Because of this assumption and also because of the inequality $h\nu_{ni,kj} \ll kT$, we have:

$$\chi - \chi_b = \chi_1 + \chi_2 ;$$

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$$X_1 = \frac{B}{kT}\sum_{n,i,j} |M_{n,i,j}|^2 f(\nu_{n,i,j}, \nu)\, e^{-E_n/kT};$$

$$X_2(\nu_{n,i,j}) = X_1(-\nu_{n,i,j}) \qquad (2)$$

$$X_b = B\sum_{n,i,k} 2\frac{|M_{n,i,k}|^2}{h\nu_{n,i,k}} e^{-E_n/kT}.$$

The quantity $X - X_b$ depends on the applied static field H because of the differences of levels h $\nu_{n,i,j}$ entering the equation (2). For the sake of simplification we shall assume the dependence of $\nu_{n,i,j}$ on H to be linear. It is true that the final conclusions are not essentially altered without this assumption.

The relations obtained in the work [1], as is known, may be derived from the fact that X is an analytical function of ν that possesses no poles in the lower half of the complex plane. The justification of this condition may easily be confirmed by the type of formula (1). However this condition is not satisfied if we consider X as function of H. The first part of the complex susceptibility X_1 consists of an analytical function of H, possessing no poles in the upper half of the complex plane; therefore the following relations between the real and the imaginary parts of this function will result:

$$X_1'(H) - X_1'(\infty) = -\frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{X_1''(H_1)}{H_1 - H}\, dH_1, \qquad (3a)$$

$$X_1''(H) = -\frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{X_1'(H_1)}{H_1 - H}\, dH_1. \qquad (3b)$$

The function X_2 possesses no poles in the lower half of the complex plane, and therefore

$$X_2'(H) - X_2'(\infty) = \frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{X_2''(H_1)}{H_1 - H}\, dH_1 \qquad (4a)$$

$$X_2''(H) = -\frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{X_2'(H)\, dH_1}{H_1 - H} \qquad (4b)$$

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It is seen from (1) and (2) that $\chi'_1(\infty) = \chi'_2(\infty) = 1/2(\chi_o - \chi_b)$. Taking this under consideration we obtain from (3) and (4)

$$\chi_o - \chi_b - \chi'(H) = \frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{\chi'_2(H_1) - \chi'_2(H)}{H_1 - H}\, dH_1 \tag{5a}$$

$$\chi''(H) - 2\chi''_2(H) = \frac{2}{\pi}\int \frac{\chi'_2(H_1)}{H_1 - H}\, dH_1 \tag{5b}$$

If the function $2\chi''_2(H)$ were known in explicit form, the relations (5), similar to Kramers' formulas, would allow us, while knowing $\chi'(H)$, to find $\chi''(H)$ and vice-versa. It may be concluded from (3) and (4) that for H varying from zero to infinity the function $2\chi''_2(H)$ decreases monotonically from the value $\chi''(0)$ to zero. Often $\chi''(0)$ is small in comparison with the values of χ'' at $H > 0$. Therefore the "zero" absorption on the resonance absorption curves is usually very small in comparison with maximum absorption in the case where the oscillator's frequency is: $\nu \approx 10^9$ cycles. In such cases the function $2\chi''_2(H)$ may be represented approximately simply by a straight line cutting on the ordinate the coefficient of "zero" absorption and coinciding with the absorption curve for large H.

In the case of resonance absorption curves having considerable "zero" absorption, we may proceed in the following way. Zavoyskiy, Kozyrev and the author suggested the following formula [3]:

$$\chi''/\chi_o = (\sqrt{\pi}/2)\left[\exp\{-[(\nu-\nu_o)/\nu_1]^2\} + \exp\{-[(\nu+\nu_o)/\nu_1]^2\}\right] \nu/\nu_1 \tag{6}$$

Here $\nu_o = \gamma\mu_o H$; $\nu_1 = 1.2\, g\mu_o\delta$; g is the gyromagnetic factor; μ_o the magneton; δ is the right half width of the absorption curve. Because of the complexity of the

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phenomenon of paramagnetic absorption, we cannot, of course, expect that formula (6) will account for all the details of the experimental curves. We may assume, however, that because of the simplicity of the function $\chi''_2(H)$ we can approximate it in a satisfactory way by the second part of formula (6):

$$2\chi''_2 = \chi''(0) \cdot \exp\left\{-\left[(\nu+\nu_i)/\nu_i\right]^2\right\} / \exp\left\{-\frac{\nu^2}{\nu_i^2}\right\} \tag{7}$$

We should remark that a number of writers [4] use for χ'' a formula which differs from (6) by absence of the second exponential term and therefore has a doubled coefficient. This abbreviated formula in the case of high frequencies $\nu \gg \nu_i$; differs from (6) only by giving to χ'' doubly large values. In [5] absolute measurements of $\chi''(H)$ were conducted on copper salts and manganese. The experimental curves agree satisfactorily just with formula (6). The inapplicability of the abreviated formula is also seen in the fact that the absorption cannot, because of considerations of symmetry, depend on the sign of the applied magnetic field. It also follows, because function $\chi''(H)$ is even, that for a field tending to zero, the absorption curve follows parallel to the axis of abscissae. This fact is important, because of the difficulties connected with absorption measurements for small values of H.

The relations (5) are reduced by means of simple transformations to a form convenient for graphical computation, with the help of experimental curves giving the main values entering in (5) as Cauchy integrals. We obtain

$$\chi_0 - \chi_b - \chi'(H) = \frac{1}{\pi}\int_0^\infty \frac{F(H+H_1) - F(H-H_1)}{H_1}\,dH_1 \tag{8a}$$

$$\ldots F(H) = \frac{1}{\pi}\int_0^\infty \frac{\chi'(H+H_1) - \chi'(H-H_1)}{H_1}\,dH_1 \tag{8b}$$

where $F(H) = \chi''(H) - 2\chi''_2(H)$. During the computation process we have to keep in mind that $F(H) = -F(-H)$ and $\chi'(H) = \chi'(-H)$. Zavoyskiy [6] was first to suggest a method of measuring the function $\chi'(H)$ at high frequencies. He obtained

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curves for $\chi'(H)$ and $\chi''(H)$ in the case of anhydrous manganese sulfate and wave-length equal to $\lambda = 16$ cm. Romanov [7] measured $\chi'(H)$ and $\chi''(H)$ for a whole series of salts of elements of the iron group at lower frequencies ($\lambda = 66$ and 217 cm). Computations showed satisfactory agreement between experimental curves and formulas (8).

In order to establish the relation between absorption curves and the value of static susceptibility, let us assume in (8a) that $H = 0$; then we get

$$\chi_0 - \chi_b - \chi'(0) = \frac{2}{\pi}\int_0^{\infty} \frac{\chi''(H)}{H}\, dH \qquad (9)$$

The high-frequency susceptibility $\chi'(0)$ is close to zero when the static magnetic field, at frequencies of a variable field large in comparison with the inverse time of relaxation, is absent. The value χ_b entering (9) is in most cases connected with the value of splitting of the levels of the paramagnetic particle in the intercrystalline electric field. If this splitting is large in comparison with kT, we may assume that $\chi_b = 0$. This happens in many compounds of elements of the iron group. But if the splitting of levels by the electric field of the crystal is comparable to kT, then χ_b may make up considerable part of χ_0. Computation shows that for a cesium ion in a field of cubic symmetry we have $\chi_b \sim 1/2\, \chi_0$, and that in a field of rhombic symmetry of the type $A(x^2 + y^2 - 2z^2)$ the value of χ_b must be: $\chi_b \sim \frac{3}{4}\chi_0$. Evidently to large values of χ_b corresponds a comparatively small effect of paramagnetic resonance absorption in alums and salts of rare earth elements. In these substances the observed effect is connected with transitions in only the strongly-populated levels; but transitions between levels, whose intervals are comparable to kT, could be observed only at optic frequencies.

In the work mentioned above [4] it was experimentally established for a number of manganese and copper salts that the areas under the absorption curve is

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$g = (\pi/2)H_m \chi_0$, where H_m is the static field at maximum χ''. Kozyrev and Salikhov [8] established as a result of their investigations of paramagnetic resonance absorption in a whole series of manganese, chromium and copper salts that χ''_{max}/χ_0 = constant. These simple empirical relations are approximate and may easily be obtained from (2) by integration of χ'' with respect to H. At low frequencies and also in the case of curves with several absorption peaks, these relations become very inaccurate.

Formula (1), from which we proceeded in our reasoning, is based on Boltzmann's statistics. In applying it to the electron gas we found it necessary to introduce the Fermi distribution function, which however will not effect the final conclusions; therefore relations (5) may be applied to metals. Finally we should remark that in all our derived formulas by "static susceptibility χ_0" we meant the purely paramagnetic part of it. Hence the experimental investigation of paramagnetic absorption of metals may be considered an interesting method of measuring the diamagnetism of the electron gas, discovered by Landau [9].

Bibliography

1. Kramers, H. A., Atti Congr. Fis. Como, 545, (1927).
2. Van Vleck, J. H. and Weisskopf, V. F., Review of Modern Physics, 17, 227, (1945); Frohlich, H., Nature, 157, 478 (1946).
3. Al'tshuler, S. A., Zavoyskiy, Ye. K., and Kozyrev, B. M., Zhurnal Eksperimental'noy i Teoreticheskoy Fiziki, 1122, (1947).
4. Pake, G. E., and Purcell, E. M., Physical Review, 74, 1184, (1948).
5. Cummerow, R. L., Halliday, D., and Moore, G. E., Physical Review, 72, 1233, (1947).
6. Zavoyskiy, Ye. K., Zhurnal Eksperimental'noy i Teoreticheskoy Fiziki, 17, 155, (1947).
7. Romanov, I. M., Dissertation, Kazan University, (1950).
8. Kozyrev, B. M., and Salikhov, S. G., Zhurnal Eksper i Teoret Fiz, 19, 185, (1949).
9. Landau, L. D., ZS fur Physik, 64, 629, (1930).

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