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Temperature modulation instead of magnetic field modulation suggests a new method for the measurement of the relaxation time T_1.

Recently a new technique[1]) has been devised for measuring paramagnetic spectra using a phase sensitive detection with temperature modulation instead of magnetic field modulation. Among the advantages of this new method, which gives directly the absorption (or dispersion) spectrum and not its derivative, there is a greater sensitivity for revealing broad lines or flat absorption bands, for which the field modulation method does not give an observable signal.

However the relaxation time T_1 may influence the signal coming from the sample. In this note its effect has been calculated and we suggest a method to measure T_1, to be employed in those situations in which the normal methods[2]) are not suitable.

The temperature is supposed to oscillate around a constant value T_0, i.e., using complex notations

$$T(t) = T_0 - \Delta T e^{i\omega t}, \tag{1}$$

$\Delta T/T_0$ is the so called modulation index. The rf susceptibility χ as a function of the various parameters can be calculated employing the Bloch phenomenological equations[3]) or the general principles of thermodynamics applied to magnetism[4]). If the Curie law is valid and $\Delta T/T_0 \ll 1$ the result is:

$$\chi(t) = \chi(T_0) + (a - ib) e^{i\omega t}, \tag{2}$$

in which a and b are:

$$a = \chi(T_0) \frac{\Delta T}{T_0} \frac{1}{1+\omega^2 T_1^2}; \quad b = \chi(T_0) \frac{\Delta T}{T_0} \frac{\omega T_1}{1+\omega^2 T_1^2}. \tag{3}$$

This result is similar to that obtained when a magnetic system is subject to a field modulation parallel to the constant external magnetic field[5]). This fact is not surprising because of the close analogy between the two methods.

At last the signal revealed in phase with the excitation, that is the real part of (1), is*:

$$S = C\chi(T_0) \frac{\Delta T}{T_0} \frac{1}{1+\omega^2 T_1^2}, \tag{4}$$

* $\chi(T_0)$ contains the term which is resonant in the external magnetic field, absorption $\chi''(H - H_0)$ or dispersion $\chi'(H - H_0)$.

where C contains the features of the spectrometer, the amplification of detecting circuit, the thermal properties of the sample, etc. Hence the effect of the relaxation time on the response to a temperature modulation is expressed by means of the $(1+\omega^2 T_1^2)^{-1}$ term.

In theory, if the frequency of modulation is swept linearly at constant temperature, it is possible to obtain the T_1 value, relative to the line of the paramagnetic spectrum fixed by the magnetic field and spectrometer frequency values. When the signal S becomes one half of its original value $\omega T_1 = 1$. But this would imply, see (4), a temperature modulation ΔT constant everywhere in the sample independent from its frequency. This condition is not generally satisfied because of the small value of the thermal diffusivity α for almost all materials.

An approximate estimate[6]) shows that in the liquid-helium temperature range, a spherical sample, radius ≈ 5 mm, does not "feel" at its center the whole temperature variations of its surface when the frequency is greater than ≈ 100 Hz. The exact value of this "cut-off frequency" is determined by the specific heat C_p and by the thermal-conductivity coefficient K; however the result for a great number of non-metallic materials changes with respect to that given above within one order of magnitude.

The fact that $\alpha = K/\rho C_p$ (where ρ is the density) is temperature independent in the liquid-helium range for insulating crystalline solids, since $K \propto T^3$ and $C_p \propto T^3$, suggests a new method for measuring the relaxation time T_1.

If, on a fixed line of the spectrum, the temperature T_0 is varied continuously, being constant the frequency ω of the modulation, one obtains a signal which is a function of T_1 and of $\chi(T_0) \Delta T/T_0$.

This last term can be eliminated if a temperature passage is repeated using a different frequency of modulation with the same "ΔT". Since the real temperature variation in the sample depends on the modulation index $\Delta T/T_0$ and on the frequency ω, the modulation index in the new passage must be varied until the same temperature variation is obtained in

the sample. The equality of the signals S in both situations in the limit $\omega T_1 \ll 1$ warrants this demand.

Theoretically any value of the relaxation time can be measured, but, because of the difficulties to modulate the temperature of the sample* at a relatively high frequency $\omega \geqslant 10^2-10^3$ Hz, this method can be usefully employed to obtain information on relaxation times greater than $10^{-2}-10^3$ sec.

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* A possible experimental method for modulating the sample temperature consists in immerging it in a liquid helium bath and then to modulate the helium temperature. This is very easy for small indexes of modulation below the λ-point, while it is more difficult above.

References

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