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Polarization of a Paramagnet by a Fast High Intensity Magnetic Field Pulse: Spin and Phonon Relaxation, Phonon Spectroscopy

by

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Résumé. — On démontre que la réponse dynamique de la polarisation paramagnétique à une impulsion rapide et intense de champ magnétique fournit des informations sur le couplage spin-phonon, la densité et la relaxation des modes de phonons et, éventuellement sur la température de transition à l’état ordonné.

Abstract. — The low temperature transient response of the polarization of a paramagnet to a fast high intensity (1 ms; 250 kG; 1/2 sine-wave) field pulse is shown to give information on spin-lattice coupling, density and relaxation of phonon modes and, sometimes, magnetic ordering temperatures.

An analysis of the response of the magnetization to a fast 1/2 wave sinusoidal field pulse can give very direct information on:

i) the field dependence of the spin-phonon coupling;
ii) the spectral density of phonon modes;
iii) the phonon relaxation;
iv) the magnetic ordering of the paramagnet.

To illustrate, we take the classic example of CuK2(SO4)2 6 H2O a simple system on which paramagnetic resonance [1] and relaxation [2] experiments have been done. Figure 2 shows the experimentally

Fig. 1. — Form of magnetic field pulse. u represents magnetic field normalised to H maximum.

Fig. 2. — Response of the polarization of CuK2(SO4)2 6 H2O at 4.2 K to field pulse of figure 1 with H maximum = 250 kG. The crosses (+) are experimental points transcribed from a photograph of the oscilloscope trace. Curve A is best fit of eq. (6) — relaxation without bottleneck-and curve B is best fit of eq. (7) — bottleneck region.
determined response of the longitudinal magnetization of a powder sample at 4.2 K to the magnetic field pulse of figure 1, obtained with the apparatus described by Allain, De Gunzbourg, Krebs and Miédan-Gros [3]. The Cu$^{2+}$ ion, neglecting hyperfine structure, is described [1] by a rhombic $S = \frac{1}{2}$ spin Hamiltonian with $g_x = 2.16$, $g_x = 2.04$, $g_z = 2.42$ for each of the two inequivalent sites and one expects the saturation magnetization for a powder sample to be $\mu_s = 1.10 \mu_B$.

It is convenient to introduce 2 reduced variables : the polarization $P = \mu / \mu_s$ and the reduced field $u = H / H_{MAX}$. $u = 1$ corresponds to a frequency of $2 \mu H_{MAX}/h \approx 760$ GHz or an energy of $\sim 37 k_B$.

From the section $0 < u < 0.4$ of the upward going (up) curve of figure 2 where the spins are trying to relax to phonons in thermal equilibrium at 4.2 K, one can deduce the strength of the spin-lattice coupling. From the section $0.6 < u < 1$ where the spins couple strongly enough to the phonons to heat them to the spin temperature (phonon bottleneck) one can deduce the density of phonon modes and the occupation numbers of these modes after contact. From the section $0.3 < u < 1$ of the return (down-curve), where the system is again bottlenecked but with the spins colder than the phonons, one can deduce the phonon occupation numbers of the modes at the instant before contact.

It might be helpful in fixing notation and concepts to glance at the schematic diagramme of figure 3. The phonon modes are classed by frequency into the groups $P(u_i) \ldots P(u_{n})$. All the $\Delta N = \rho_u \Delta u$ modes of a group of width $\Delta u$ are supposed to be characterized by the same occupation number $n(u)$. In thermal equilibrium these $n$ are related by the Bose-Einstein distribution function; this internal equilibrium is brought about by phonon-phonon interaction (principally elastic anharmonicity) which we characterize very roughly by a rate $W_{\rho_u}(u)$ at which a mode of frequency $u$ comes into equilibrium with all the others. This is indicated schematically by the box around the phonon columns. The magnetic field sequentially tunes the spins $S$ into resonant contact with the phonon groups (path D). Simultaneously non-resonant contact is assured by the Raman processes (path Ra). Finally the phonons have a relaxation path (P-B) to the external thermostat (Bath).

If the direct process for spin-phonon contact dominates

$$\frac{dP}{dt} = -\frac{\gamma}{2} [(2 n + 1) P - 1]$$  \(1\)

where $n = n(u)$ is the phonon occupation number at the Zeeman frequency, $u$, and $\gamma = \gamma(u)$ is the spin-lattice coupling at that frequency. Further, if the phonon relaxation is sufficiently slow that energy is conserved during the time of contact between a packet of phonons and the spins

$$\rho_u \Delta u \delta n = \frac{1}{2 R} \delta P$$  \(2\)

$\rho_u \Delta u$ is the number of phonon modes in the packet of width $\Delta u$ and $\rho_u$ the density of modes normalized to the total number of chemical formulae in the sample; $R^{-1}$ is the proportion of paramagnetic centres per formula; $\delta n$ and $\delta P$ are the changes in $n$ and $P$ during contact. During the time of contact (Van Vleckian conversation)

$$\Delta \tau = \Delta u \left| \frac{\partial u}{\partial t} \right|$$

the phonon occupation numbers change by

$$\Delta n = \left( \frac{1 - P}{2 P} - n_o \right) (1 - \exp - \sigma)$$  \(3\)

where $n_o = n_o(u)$ is the occupation number just before contact, $\sigma = \frac{\gamma P \Delta \tau}{2 R \rho_u \Delta u}$ and $P$ is supposed not to vary appreciably in this interval.

Putting (3) into (2) and taking the limit $\Delta u \to 0$ we find two easily tractable limits:

(a) $\sigma \ll 1$, negligible phonon heating

$$\frac{dP}{du} = \frac{\gamma}{2} \delta u \left( 1 - (2 n_o + 1) P \right)$$  \(4\)

i.e. eq. (1) for unheated phonon system.

(b) $\sigma \gg 1$, phonon bottleneck

$$\frac{dP}{du} = \pm R \rho_u \left( \frac{1 - P}{P} - 2 n_o \right)$$  \(5\)
where the upper sign is for $\frac{\partial u}{\partial t} > 0$ and the lower one for $\frac{\partial u}{\partial t} < 0$. The resonant (conversing) phonons have been heated to the instantaneous spin temperature during passage.

For a Kramers ion like Cu$^{2+}$, $\gamma = b u^3 \rho_u$ where $b$ is a constant characterizing the spin-deformation potential. The Debye approximation for the density of phonon modes gives $\rho = 9 u^7/\mu_D^2$; it will be evident when we use this in what follows by the appearance of $\mu_D$, the Debye limit in terms of our reduced variable. Now if $\sigma \ll 1$ and $2 n_0 P \ll 1 - P$ (valid for the first portion of the up-curve where $P$ never catches up to its equilibrium value), eq. (4) integrates to

$$P(u) = 1 - \exp \left( -\frac{b}{2} \int \left( \frac{\partial u}{\partial t} \right)^{-1} u^3 \rho_u \, du \right) \approx$$

$$\approx \frac{3}{4} b u^6/\mu_D^2 \frac{\partial u}{\partial t} + C_D . \quad (6)$$

The left hand curve, A, of figure 2 represents the best fit of relation (6) to the experimental results in its range of validity ($u \approx 0.38$, see below). In the bottlenecked limit, $\sigma \gg 1$, and when $2 n_0 P(1-P) \ll 1$ (a good approximation for the up-curve where $n_0 \approx \exp - u/\mu_T$, $\mu_T \approx 1/7$ being the temperature in terms of the reduced variable) eq. (5) for $\partial u/\partial t > 0$ integrates to

$$- P - \ln (1 - P) = R \int \rho_u \, du \approx$$

$$\approx 3 R u^3/\mu_D^2 + C_D . \quad (7)$$

This relation is the right hand curve B of figure 2 and is seen to hold very well for $u \approx 0.55$.

We note that $\sigma$ may be written

$$\sigma = b u^3 P/2 R \frac{\partial u}{\partial t} \approx$$

$$\approx \left( 3 b/4 \mu_D \frac{\partial u}{\partial t} \right) (3 R/\mu_D^2)^{-1} 2 u^3 P . \quad (8)$$

where the two bracketed expressions are experimentally determined from fitting relations (6) and (7). Numerically, for this experiment, $\sigma \approx 100 u^3 P/\rho$. $\sigma \approx 1$ is seen to occur at $u \approx 0.38$ for the up-curve. This criterion agrees quite well with the upper limit for relation (6), but one finds that $\sigma = 10$ before relation (7) starts to hold well. We note that the value obtained for $b/\mu_D^2$ from fitting eq. (6) on figure 2 would give a spin lattice relaxation time at low fields of $1/T_1 = n_0(1 + \frac{1}{2}) \approx 9 b u^6 \mu_T/\mu_D^2 = 0.31 \times 10^{-4}$ H (kG)$^4$ $T \approx 0.26 \times 10^{-2}$ T. s$^{-1}$ at the frequency $v = 9455$ MHz where Gill [2] found $1/T_1 = 2 \times 10^{-2}$ T. s$^{-1}$. It is interesting to note that Stoneham's [4] theoretical estimate is about $0.8 \times 10^{-4}$ H (kG)$^4$ T. s$^{-1}$. Finally, from the fit of relation (7) shown on figure 2, we deduce that $\mu_D = 1.38$ (or $\theta_D = 51$ K) a value to be compared with $\theta_D = 103$ K deduced from the specific heat measurements of Hill + Smith [5] on the Zn ammonium Tutton salt.

It is interesting to analyze the $\sigma \gg 1$ portion of the down-curve using eq. (5) directly in its differential form to extract the phonon occupation numbers, $n_0(u)$, just prior to this second contact with the spins; one can then see to what extent they have relaxed, since the upward-going contact, where they had been prepared with $n(u) = (1 - P)/2 P$ (instantaneous spin temperature = local phonon temperature). The result, using the $\rho_u$ derived from the up-curve, is shown on figure 4, together with the occupation numbers created on the up-swing. One sees that the $n_0(u)$ are not described by a Bose Einstein function indicating that the collection of phonons has not yet relaxed to a common temperature. The

![Fig. 4.](image_url)

FIG. 4. — Occupation number of phonon modes versus reduced frequency $u$ ($u = 1$ corresponds to 37 K or 760 GHz). UP is preparation by spin contact on up-swing, $n = 1 - P/2 P$; DOWN is measurement by spin contact on down-swing, using eq. (5). BE is the Bose-Einstein distribution for reduced temperature $u_T = 0.35$; i.e. $T = 13$ K. The experimental scatter is indicated by the error flags.

$\sigma \ll 1$ portion of the down curve should reflect the spin lattice relaxation, but now the Raman $T^0$ relaxation dominates, for the lattice is much hotter than at the outset. From the slope as $u \to 0$, we deduce that $1/T_1 \sim 2.10^3$ s$^{-1}$ indicating a lattice temperature $T_L \approx 10$ K if one uses Gill's [2] results. We can also estimate the lattice temperature from $C_1$, supposing negligible the lattice bath heat exchange viz.

$$\frac{1}{2} \int u \, dP = \int_{4.2}^T C_1 \, dT .$$

This gives $T_L \approx 18$ K using the $C_1$ results of Hill [5] or 11 K using the value of $\theta_D$ deduced from our up-curve measurements.
To what extent are our starting hypotheses verified or even reasonable? At first sight it is disturbing that the spin-lattice coupling deduced from the first portion of the up-curve is smaller than what Gill [2] measured by pulse saturation on the diluted paramagnet. It will be recalled however that these measurements treat a single, and rather low (10 GHz), frequency where a concentration dependent mechanism was also present. This latter term very likely has a weaker field dependence than the Van Vleck term and so would be unimportant at high fields. The fact that the order of magnitude of the coupling that we measure is about the same as the zero concentration limit of Gill — and perhaps even that it agrees rather better with Stoneham’s [4] estimate — gives confidence in the value, quite apart from its having the expected field dependence. Rather similar discrepancies between low and high field measurements were found by Soetman et al. [6] for the Cu-Cs Tutton Salt. The bottleneck portion calls for more caution. That \( \sigma = 10 \) before this regime is well obeyed may be due to unequal coupling to different phonon modes of the same frequency and we must satisfy the bottleneck condition for all the phonons for our simplified treatment to work. More disturbing is the low value for \( \theta_0 \) (\( \approx 50 \) K instead of the 100 K deduced from the specific heat of the very similar Zn ammonium Tutton Salt [5]). On the other hand the fit to the form of eq. (7) is extremely good. We note (a) that an additional heat reservoir with a Debye type phonon spectrum could resolve this discrepancy (sample container?) and (b) that the effect of a leak from the phonon packet during the contact time \( \Delta \tau \) is to increase \( R \to R(1 + W_L \Delta \tau) \) where \( W_L \) is the leak rate per phonon. If \( W_L \) is a phonon-phonon rate, \( W_{\text{p-p}} \sim u^\alpha \) where \( 1 < n < 4 \) [7]; when \( W_L \Delta \tau \gg 1 \) an additional \( u \) dependence is introduced. Experimentally this is not so and we conclude that \( W_{\text{p-p}} \Delta \tau \ll 1 \), but we cannot rule out an \( u \) independent rate.

The assumptions are rather shakier for the down-curve. \( W_{\text{p-p}} \Delta \tau \ll 1 \) is \textit{a priori} less certain now that a broad band of phonons has been created both above and below in frequency. Such a leak would decrease the importance of \( dP/du \) in evaluating \( n_0(u) \), but since \( W_{\text{p-p}} \sim u^\alpha \) it would tend to accentuate the rise of \( n_0(u) \) for low \( u \) so increasing the deviation from a Bose-Einstein function which is already such that the \textit{temperature} is higher at lower \( u \) (if there were fast phonon-phonon relaxation, the temperature would decrease with \( u \) on the return, since energy is returned to the spins; in fact, it appears still to be heating as if the energy redistribution were not yet complete). There is, then, some evidence that the hypotheses are not too wrong even for the return curve.

Similar experiments [8] on MnSO\(_4\) 4 H\(_2\)O and Mn(NH\(_4\))\(_2\)(SO\(_4\))\(_2\) 6 H\(_2\)O gave qualitatively similar curves except for two features not visible in the Cu case: a low plateau in the up-curve when \( H > H_{\text{LOC}} \) showing the existence of a local field randomly distributed and an abrupt fall off towards zero of the magnetization on the return curve for \( H < H_r \) which reflects spin ordering as the spin system is cooled. This is in accordance with the very different values of exchange coupling in the two salts [9, 10]. The bottleneck region, however, is rather more difficult to analyze as a result of the simultaneous action of phonons of frequency \( u \) and \( 2u \) in the relaxation of such multilevel systems.

Quite apart from providing an interesting demonstration of spin cooling from 4 K to \( < 0.1 \) K in lms, this relatively simple experiment yields a considerable wealth of physical information: spin-phonon coupling as a function of field, density of phonon modes, information on phonon relaxation, local fields and ordering temperatures. One can easily conceive of using the features described to detect low lying optical phonon modes or to measure electronic transition energies by their resonant phonon relaxation.

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References