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SOME RECENT RESULTS ON PARAMAGNETIC SPIN-LATTICE RELAXATIONS IN HYDRATED COBALT, MANGANESE AND CHROMIUM SALTS

C. J. Gorter and A. J. van Duyneveldt

Kamerlingh Onnes Laboratory, State University of Leiden,
Nieuwsteeg 18, Leiden, The Netherlands

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The Editorial Board of Revista Mexicana de Física wants to pay homage to Professor C. J. Gorter for his many contributions to science on the occasion of his retirement as the Director of the Kamerlingh Onnes Laboratory, one of the most important Low Temperature Research Centers in the world. For this reason we invited Professor Gorter to write a short review paper about his most recent work. Also, one of his close collaborators Dr. A. J. van Duyneveldt agreed to write a short historical introduction about "Gorter's Hobbies".

Dr. Ariel A. Valladares
Director

PRELIMINARY WORDS

by

A. J. van Duyneveldt

GORTER'S HOBBY

Some historical comments about the contributions to physics of C.J. Gorter followed by a review on spin-lattice relaxation in hydrated cobalt, manganese and chromium salts.

1. INTRODUCTION

In November 1973, C. J. Gorter retired as professor and director of the Kamerlingh Onnes Laboratory in Leiden. The present paper is written to focus attention on his wide interest in physics. Gorter showed a versatility that is hardly possible at the present time with its high specialisation. For young scientists it is interesting to know that he made essential contributions to the development of many fields in physical science. We shall try to mention the most striking items in the first part of this paper. In the second part we want to discuss in more detail a few aspects of paramagnetic relaxation, a subject that in the Kamerlingh Onnes Laboratory is known as Gorter's hobby.

2. HISTORICAL REMARKS

From 1924 to 1930 Gorter was a student at Leiden University. During these years he showed a large scientific as well as non-scientific activity. He joined two eclipse expeditions, one to Atjeh (Indonesia) and one to Norway (on bicycle); also he was active in the socialist student organisation and the student faculty. In 1932 Gorter received his Ph.D. on a thesis called: ***Paramagnetische Eigenschaften von Salzen***; his promotor was Prof. W. J. de Haas[1]. During his student years, he was strongly influenced by Prof. Paul Ehrenfest and in fact Ehrenfest guided him to choose his first scientific work after the completion of his thesis. Ehrenfest had pointed out in 1920, that an interaction with thermal motion is essential to obtain an equilibrium magnetization in a paramagnetic substance[2]. As a continuation of the unsuccessful experiments of Breit[3], Gorter tried to detect paramagnetic relaxation during his stay at A. D. Fokker's laboratory at Teylers foundation in Haarlem. Although he learned a lot about radio techniques, it was 1936 before he met with success[4]. The positive experiment in which the existence of an imaginary susceptibility (χ'') was demonstrated, if a strong radio-frequency field acts on a paramagnetic substance, was carried out at low temperatures. Concerning his stay in Haarlem, Gorter writes:

> "In the quiet atmosphere of Haarlem I have, following the example of De Haas, carried out without success several simple but rather fantastic experiments, including attempts to detect nonlinear optics with concentrated sunlight, to detect a universally present neutron gas, to observe an electronic Raman effect, to concentrate the heavy component in water by biological means, etc. In the mean time, I pondered simple theoretical problems with H. B. G. Casimir, A. D. Fokker, E. C. Wiersma and L. Nordheim."

After this period Gorter was appointed reader at the University of Groningen, where he completed the discovery of paramagnetic relaxation, in collaboration with his student F. Brons, by investigating also the real component of the differential susceptibility (χ').[5] The Swedish theoretical physicist I. Waller, proposed an excellent theoretical analysis of paramagnetic relaxation in 1932.[6] The experiments of Gorter showed the importance of this theory, together with the extensions put forward by R. Kronig[7], J. H. Van Vleck[8] and others. In fact, this work stimulated 21 young investigators between 1938 and 1974 to write theses on this subject with Gorter as research director.

Also in 1936, Gorter tried to observe nuclear magnetic resonance in lithium fluoride. At the proper value of the external magnetic field, transitions between the nuclear energy levels are stimulated by a high frequency field and absorption of energy was expected. In a short paper he announced the negative result[9]; the rise in temperature of the sample was not seen, the failure being due to the poor heat contact between the nuclear spins and the lattice. However, his basic ideas about nuclear magnetic resonance were correct and after he visited Rabi in New York, in 1938, the discovery of nuclear magnetic resonance was only a question of a few months[10]. Gorter writes about this discovery:

> "I cannot deny that I felt some pride, mixed with the feeling that my contribution had been somewhat undervalued though my advice was acknowledged in the Letter. I realized quite well, however, that it would have cost us years to set up the adequate equipment in our small group at Groningen".

In 1940 Gorter was appointed as Pieter Zeeman's successor at the University of Amsterdam where he built up a small but able research team with people such as Broer, Volger, De Groot and Dijkstra. In spite of the difficulties during the war, this group made several attempts to discover electron spin resonance, first with the paramagnetic relaxation equipment and later with a small 10-cm klystron, secretly placed at their disposal from Philips in Eindhoven. The experimental technique was primitive and the results were called negative. A re-examination of the data, after the discovery of ESR by Zavoisky in the Soviet Union[11], showed that some indications of weak absorption maxima were present in those early experiments. During the winter of 1944-45 hardly any experimental work was possible in Amsterdam. Gorter spent his time writing his well known book: *Paramagnetic Relaxation*, in which he summarized the many interesting problems, solved and unsolved, of this field[12]. Since that time many experimental results have been obtained and the measuring techniques have been refined, but Gorter's book is still used as a general reference for an introduction in this field.

During this same period Gorter noted that the hyperfine interaction between the electrons and the atomic nuclei would be suitable to orient the nuclei at low temperatures. In 1946 Gorter became professor and director of the Kamerlingh Onnes Laboratory in Leiden, his energy and organisational talent were a great stimulus to make up for the scientific arrears of the war. One of the projects was the study of oriented nuclei with Steenland, Poppema, Huiskamp and Postma. The start was slow, so in 1948, at the Paris conference in commemoration of Jean Perrin and Paul Langevin, he could only mention the basic idea[13]. The Leiden researches about anisotropy of gamma rays emitted by ^{59}Fe and about the absorption of neutrons by Gd and Sm were very doubtful[14]. It was known that at the Clarendon Laboratory in Oxford similar experiments were being performed. The hyperfine structure of electron spin resonance was discovered in Leiden by a guest from Oxford, R.P. Penrose[15]. This discovery played an important role in the further developments and in 1951 the Oxford group observed the anisotropy of ^{60}Co gamma rays[16], a few weeks before the Leiden group[17]. The anisotropy of beta emission was more difficult to study. In contrast to gamma rays, beta particles cannot easily pass the walls of a cryostat. In 1952 Gorter suggested that for positron emission this difficulty could easily be circumvented by observing the annihilation gamma rays of the positrons. About this suggestion Gorter tells the following anecdote:

> "When in 1954 a very able young foreign physicist, who intended to work for a year in Leiden, asked me for a research subject, preferably in our adiabatic demagnetization group, I proposed to him that he could

> try to observe the anisotropy of positrons emitted by oriented nuclei, making use of the coincidence of the two annihilation gamma rays. He wished to take theoretical advice first, and then raised well formulated objections based on the expectation that the intensity of allowed beta radiation in opposite directions would be equal, while, for the few positron emittors which could be oriented, anisotropic forbidden radiations would be very feeble. When I insisted, reminding him of the discovery of the Zeeman effect in 1896, in spite of H. A. Lorentz's conclusion from the known e/m ratios, that the expected separations would be too small to be observable, he simply retorted: "I refuse to waste my time in useless experiments". He then chose to carry out another and quite interesting investigation, but he had missed the youthful acquisition of fame, as became clear when T. D. Lee and C.N. Yang[18] two years later demonstrated that the assumption that parity must be conserved in allowed beta emissions, which therefore should be equal in intensity in opposite directions, was not founded."

Then in Leiden experiments on ^{58}Co positrons were carried out and a considerable anisotropy was observed[19]. A similar experiment was performed a few weeks earlier by Prof. Wu and co-workers[20] for the asymmetry in the electron emission of ^{60}Co and one could conclude that parity is not conserved in the case of weak coupling.

In 1952, during their studies of the magnetic properties of a single crystal of $CuCl_2.2H_20$ with proton resonance, Poulis and Hardeman observed an orientation dependence, suggesting that this salt becomes antiferromagnetically ordered below 4.3 K.[21] This way of ordering was suggested in 1932 by Néel[22]. It was Gorter who stimulated a lot of interesting researches on this salt. Apart from nuclear resonance, the static[23] and the differential[24] susceptibility, the relaxation[25] and the specific heat[26] were studied. Gorter and Haantjes[27] developed a theoretical model for the antiferromagnetic behaviour that was extended for some special cases later. As a result, an excellent description of the antiferromagnetic properties was obtained, with $CuCl_2.2H_20$ as an example but also as a starting point for many further researches in this field.

Another subject that interested Gorter was superconductivity. In 1947 he proposed some ideas to understand the so-called ***intermediate state***[28]. In 1960 investigations were started to demonstrate the quantization of the flux encircled by a superconductor as predicted by Fritz London in 1948. The experiments were hindered by noise, nevertheless flux jumps of the order hc/e were observed. Before any progress in the measuring technique in Leiden was realised, the Stanford and München groups announced their successful results of a flux quantum half as large as was predicted by London[29].

Up till now we did not mention Gorter's qualitative explanation of the Senftleben effect[30], his work on liquid helium together with Mellink[31], the collaboration with is friend Van Vleck leading to the publication on exchange narrowing of resonance lines[32] and of course the many new developments on relaxation phenomena. The above comments are a rather personal choice out of a lot of interesting publications and we do not intend to be complete. Just one more activity must be mentioned. Gorter edited the series *Progress in Low Temperature Physics* of which six volumes were published and in which many experts wrote review articles about various aspects of low temperature physics.

Let us now consider in more detail one of the topics that interested Gorter for so many years: paramagnetic spin-lattice relaxation.

SOME RECENT RESULTS ON PARAMAGNETIC SPIN-LATTICE RELAXATIONS IN HYDRATED COBALT, MANGANESE AND CHROMIUM SALTS

C. J. Gorter and A. J. van Duyneveldt

The first suggestions and attempts to study magnetism by oscillating magnetic fields were made by Lenz[33], Ehrenfest[2] and Dorfman[34] in the early twenties. A thorough theoretical study performed by Waller[6] pointed out the existence of two types of paramagnetic relaxation phenomena: spin-spin relaxation and spin-lattice relaxation. In the first case a thermal equilibrium between the paramagnetic spins is established by means of the interactions among them. In the second case the interaction between the spins and the lattice oscillations achieve the thermal equilibrium in the system. As mentioned above, experimentally, an interesting step forward was made in 1936 by Gorter[4]. It enabled the discovery and study of the paramagnetic relaxation in a constant magnetic field on which an oscillating field was superimposed. The first measurements were made at frequencies of the order of 10^6 Hz. Later the experimental facilities were gradually broadened towards a frequency range from 10^{-1} to 10^{10} Hz. In this period, based on the rapid development of radio frequency electronics, three new fields of experimental research were opened: transversal nuclear magnetic resonance, transversal electron spin resonance, and longitudinal electron spin relaxation.

In the present review we shall discuss some topics of longitudinal electron spin relaxation (paramagnetic relaxation). This phenomenon has been observed and studied by many Dutch physicists in Groningen, Amsterdam and later mainly in Leiden. The theses of Brons, Teunissen, Dijkstra, Broer, Volger, Bijl, De Vrijer, Van der Marel, Bölger, Van den Broek, Verstelle, Locher, De Vries, Drewes, Van der Molen, Van Duyneveldt, Roest, Verbeek, Hillaert and Soeteman show the gradual extension of the experimental facilities and the consequent increase in understanding of the phenomena.

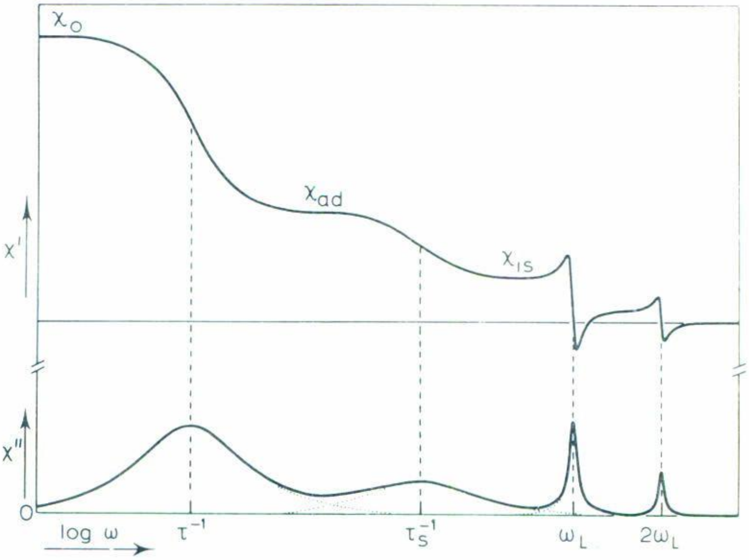

Fig. 1 Schematic diagram of the real and imaginary part of the parallel susceptibility (χ' and χ'' respectively) as a function of the logarithm of the angular frequency.

Figure 1 is a sketch of the real part χ' and the imaginary part χ'' of the parallel susceptibility, as a function of the logarithm of the angular frequency ω for a system with $S = \frac{1}{2}$. The first decrease represents the effect of spin-lattice relaxation, which causes the susceptibility to drop from its initial (isothermal) value χ_0 towards the adiabatic value χ_{ad}. The relaxation time τ connected with the relevant mechanism can be found from this plot because $\tau = \omega^{-1}$ for the maximal χ''- value and for the point of inflection of the χ'-curve (Casimir and Du Pré[35]). Spin-spin relaxation effects cause the susceptibility to decrease to χ_{is} in a similar way, while at higher frequencies two resonance bands can be observed, one at the common perpendicular resonance frequency and one at twice that frequency. When the parallel magnetic field is increased the two resonance bands move to the right; the spin-spin relaxation rate (τ_s^{-1})

moves rapidly to the left, the overlap of the energy levels for which the magnetization is parallel and antiparallel to the external field, disappearing exponentially.

We will now restrict ourselves to the behaviour of the paramagnetic spin-lattice relaxation time as a function of temperature and external magnetic field. The relaxation times to be discussed have all been obtained by a non-resonance technique in which χ' and χ'' are measured instantaneously[36]. By means of two electronic set-ups, the frequency range between 0.1 Hz and 1 MHz is covered and we are able to detect relaxation phenomena if τ lies between 10 and 10^{-7} s.

I. SPIN-LATTICE RELAXATION PHENOMENA IN SOME HYDRATED COBALT SALTS

The ground state of Co^{2+} ions in the samples considered is a so-called Kramers doublet[37]. The next highest doublet is situated at $\Delta \gg kT$, $k\theta_D$ (θ_D being the Debye temperature, which is related to the maximum frequency ω_m of the system of lattice oscillations by $k\theta_D = \hbar\omega_m$). This means that the lattice oscillations (phonons) cannot excite the cobalt ions into the next highest energy state, so the paramagnetic relaxation properties at low temperatures can be described adequately on the basis of a simple $S = \frac{1}{2}$ system.

The two processes that enable an isolated paramagnetic ion to exchange energy with the lattice are schematically indicated in figure 2. In the direct process the energy ΔE is conserved by creating a phonon $\hbar\omega$ (or reverse);

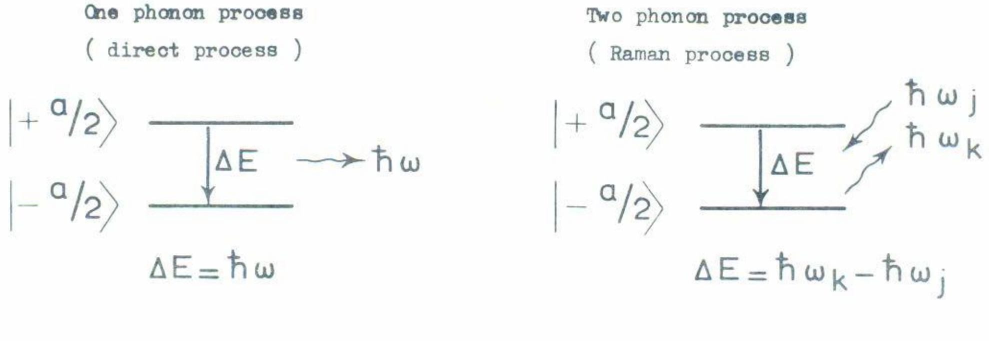

Fig. 2

the two phonon process (or Raman process) takes place by annihilating a phonon $\hbar\omega_j$; and creating another phonon $\hbar\omega_k\,(=\hbar\omega_j+\Delta E)$ (or reverse). To calculate the time constant with which the magnetization reaches its equilibrium value after an external disturbance, one must consider the transition probabilities $w_{|+a/2>\to|-a/2>}$ and $w_{|-a/2>\to|+a/2>}$. These quantities equal w if $\Delta E \ll kT$; for the experimentally interesting circumstances τ is $2w^{-1}$.

From the general expression for the transition probability one may derive the following (simplified) expression for the spin-lattice relaxation time[38] :

$$\tau^{-1} = \underset{\text{(direct process)}}{ATH^4} + \underbrace{B_1T^9H^0J_8(\theta_D/T) + B_2T^7H^2J_6(\theta_D/T)}_{\text{(Raman processes)}} \quad (1)$$

This expression is correct if the splitting within the doublet due to the external magnetic field ($g\beta H$) is smaller than kT. The term $J_n(\theta_D/T)$ is one of the integrals:

$$J_n(\theta_D/T) = \int_0^{\theta_D/T} [\,x^n \exp x/(\exp x-1)^2]\,dx \qquad (2)$$

where $x = \hbar\omega/kT$. These integrals cause the temperature dependences of the Raman relaxation times to vary from $\tau^{-1} \propto T^2$ at high temperatures towards $\tau^{-1} \propto T^{n+1}$ if $T \ll \theta_D$. From eq. (1) it seems interesting to study τ as a function of external magnetic field and temperature in order to get information about the various relaxation processes. However, especially in magnetically concentrated materials the situation is more complicated. Particularly in weak external magnetic fields the magnetic ions cannot be considered as isolated from each other. In general, interactions between the magnetic ions cause a shortening of the relaxation time. For Raman processes these effects are quite well described by the phenomenological Brons-Van Vleck relation[39]. The direct process can be short circuited by a number of other processes as for instance cross-relaxations[40], impurity relaxations[41] and Temperley processes[42].

The experimental investigation on cobalt salts was started in 1956 by Haseda[43] who examined the relaxation times of $Co(NH_4)_2(SO_4)_2.6H_2O$ at $T = 4.2K$. At external magnetic fields above 300 Oe the relaxation time decreases but by no means the H^{-4} dependence of eq. (1) was observed (figure 3). Van den Broek and Van der Marel[44] enlarged the field range towards 4 kOe and discovered for $CoX_2(SO_4)_2.6H_2O$ where X was NH_4, K or Cs an increase of τ at the magnetic

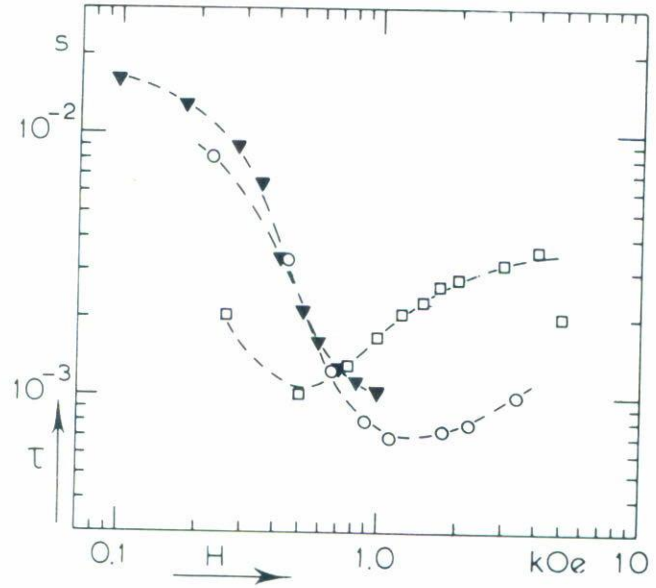

Fig. 3 Relaxation time τ against external magnetic field H at T = 4.2K; results from early reports.

▼ Haseda[43], Cobalt ammonium Tutton salt

○ Van den Broek[44], Cobalt ammonium Tutton salt

□ Poolman[59], Cobalt cesium Tutton salt.

fields above 2 kOe (figure 3). The field value where the increase started was slightly dependent on the choice of the sample. A positive slope in the log τ - log H diagram cannot be explained by one of the mechanisms of eq. (1). De Vries[45] examined the relaxation times of a series of the above mentioned cobalt Tutton salts more thoroughly. He found a large number of distinct field values where the spin-lattice relaxation times were relatively short compared to the times at slightly different fields. This kind of phenomena suggests that cross-relaxations may play a role in the relaxations. Wharmby and Gill[46] were able to explain most of the anomalies by assuming a few percent of nickel ions to be present as impurity in the cobalt Tutton salts. Nickel ions do exhibit quite fast spin-lattice relaxation times and therefore can be very effective as an energy exchange path for the cobalt ions. Of course the effectiveness of such a process is directly related to the coupling between the nickel and cobalt ions, in other words to the cross relaxation processes[40] which are only possible at discrete external magnetic field values. Knowing these complicated weak field results, Roest[47] investigated some cobalt salts in external magnetic fields up to 50 kOe. These fields became available for the study of paramagnetic relaxations because of the availability of super-

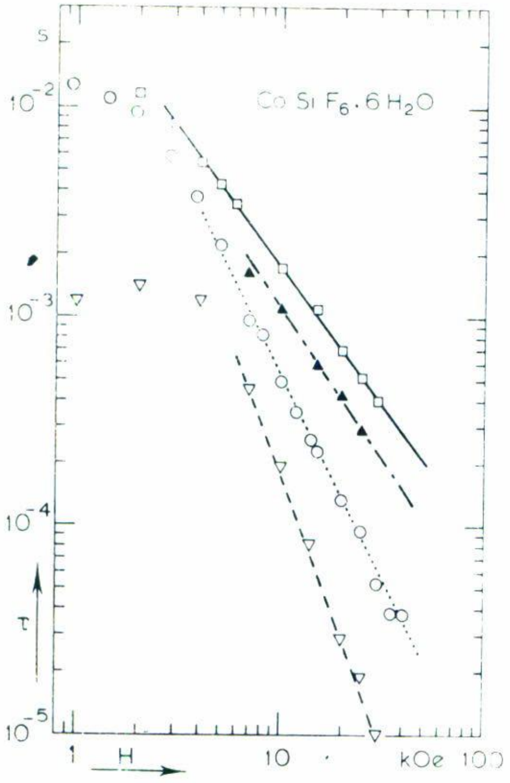

Fig. 4 Relaxation time versus external magnetic field for various powdered samples of $CoSiF_6.6H_2O$ at $T = 2.1K$.

□ average crystal diameter 2 mm;

Δ: 0.4 mm; ○: 0.1 mm; ∇ : 0.03 mm.

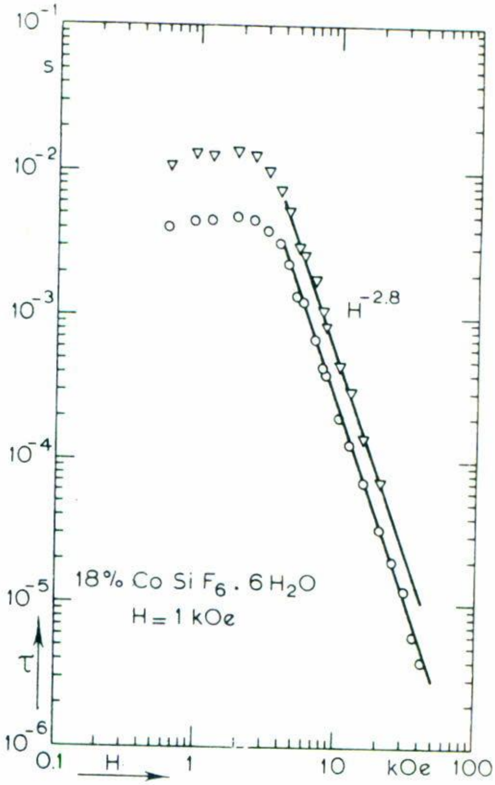

Fig. 5 Relaxation time versus external magnetic field for powdered $Co_{0.18}Zn_{0.82}SiF_6.6H_2O$ (average crystal diameter 0.1 mm)

○ : $T = 4.2$ K; ∇ : $T = 2.1$ K.

conducting magnets. A first result is shown in figure 4 for $CoSiF_6.6H_2O$. Above 4 kOe the relaxation times become considerable shorter, which indicates the possibility of observing the first term of eq. (1). However, the slope of the log τ - log H curve does not reach -4, as predicted theoretically. Presumably, at these strong fields another interesting complication occurs. In the case of relaxation due to the direct process, the magnetic spin-system exchanges energy with the lattice oscillations of certain frequency ω. The lattice oscillations are in thermal contact with the surrounding helium bath. It is quite possible that the coupling between the phonon system and the cooling liquid is inadequate to maintain thermal equilibrium between these two systems[48]. One possible way to check whether this is the case, is to observe the relaxation times of various samples consisting of small crystallites. The smaller the average crystal diameter, the better the heat contact between the phonon system and the cooling liquid. Therefore one expects these phonon bottleneck effects to disappear by reducing the crystal size. This effect is illustrated by the measurements in figure 4, where a series of four different samples is shown. But even the smallest average crystal dimensions that could be realised do not show $\tau \propto H^{-4}$. Another possible way to overcome phonon bottleneck effects is to replace part of the magnetic ions by non-magnetic ions; this reduces the energy content of the spin-system instead of increasing the heat contact between phonons and cooling liquid. The effect is similar to that shown in figure 4. A cobalt fluosilicate sample in which 82% of the cobalt ions is replaced by zinc ions shows $\tau \propto H^{-2.8}$ (figure 5). A sample of $Co_{0.02}Zn_{0.98}K_2(SO_4)_2.6H_2O$ even shows $\tau \propto H^{-4}$ (figure 6).

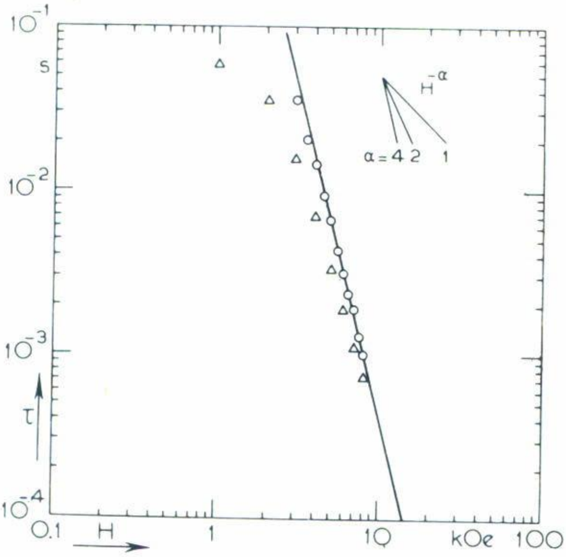

Fig. 6 Relaxation time versus external magnetic field for powdered $Co_{0.02}Zn_{0.98}(NH_4)_2(SO_4)_2.6H_2O$.
○ $T = 2.1$ K; △ $T = 4.2$ K.
The drawn line exposes $\tau \propto H^{-4.0}$.

The measurements in the figures 4 to 6 demonstrate the experimental difficulties in verifying the direct relaxation process. We developed a method to derive the coefficient A of the direct process (eq. (1)), even from a series of measurements such as those shown in figure 4. At weak fields the relaxation times observed are usually shorter than the time associated with the direct process, due to cross-relaxation[40] impurities[41], etc. At strong fields the phonon bottleneck effects lengthen the relaxation times observed to values larger than the direct process relaxation times. This means that there must be an intermediate field value for which the observed relaxation time is equal to the relaxation time of the direct process. From a close analysis of the shape of the χ' and χ'' versus frequency curves at various external fields one can derive this intermediate field value[47]. A few of the results obtained in this way for the coefficient *A* of the direct process for several cobalt salts are given in table I.

TABLE I

Coefficient *A* of the direct process for several cobalt salts*

Sample	$A\,(s^{-1}K^{-1}kOe^{-4})$
$CoSiF_6.6H_2O$	0.06 – 0.24
$Co_{0.05}Zn_{0.95}SiF_6.6H_2O$	0.12
$Co(NH_4)_2(SO_4)_2.6H_2O$	0.04 – 0.11
$CoK_2(SO_4)_2.6H_2O$	0.06 – 0.17
$CoCs_2(SO_4)_2.6H_2O$	0.3 – 0.5
$Co_3La_2(NO_3)_{12}.24H_2O$	0.1 – 0.7

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*If a range of values is indicated, the value of *A* varies slightly, depending on the chemical purity and the average diameter of the crystals in the powder.

The experiments described above were all concentrated on the determination of the direct spin-lattice relaxation process. At the same time the second term of eq. (1) was verified in many experiments. The Raman process is not sensitive to impurities, etc., while phonon bottleneck effect, do not play a role as this mechanism involves all phonon modes, so the energy content of the phonon system is much larger. In fact the field independent Raman process was observed at temperatures above 4 K, in weak external magnetic fields. A few examples are shown in figure 7 and 8. One may notice the varying slope of the curves at the higher temperatures due to the influence of the integral $J_8(\theta_D/T)$.

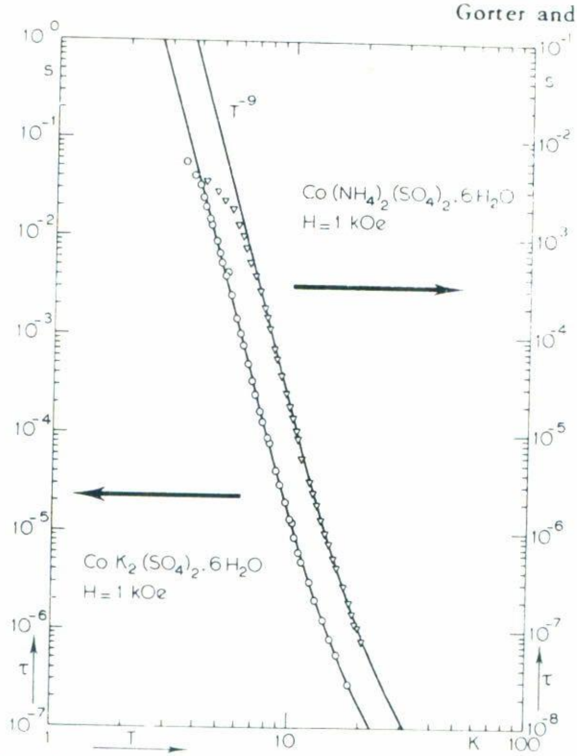

Fig. 7 Relaxation time versus temperature for powdered $CoK_2(SO_4)_2.6H_2O$ (circles left scale) and $Co(NH_4)_2(SO_4)_2.6H_2O$ (triangles, right scale) at an external magnetic field of 1 kOe.

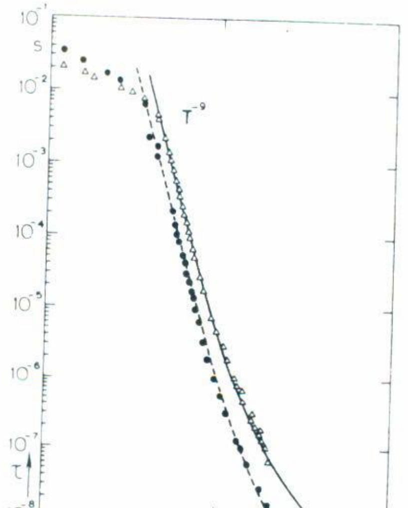

Fig. 8 Relaxation time versus temperature for powdered $CoSiF_6.6H_2O$ (circles) and $Co_{0.18}Zn_{0.82}SiF_6.6H_2O$ (triangles) at an external magnetic field of 1 kOe.

The third term of eq. (1) was predicted by Kronig[49] as early as 1939. Up till 1972 experiments never showed this temperature and field dependent Raman relaxation process. In fact one usually observes only one of the terms of eq. (1) because this term is more effective than the other possibilities under the experimental conditions. The availability of a superconducting magnet with a separate inner cryostat allowed us to examine the relaxation times at temperatures between 14 and 20 K up to 50 kOe. Under these conditions we were able to demonstrate the existence of the field dependent Raman relaxation process in cobalt Tutton salts[50]. Figure 9 shows such an experimental result; below 10 kOe one observes the field independent T^9 Raman process, above this field the relaxation times tend towards the H^{-2} field dependence of the H^2T^7 Raman process.

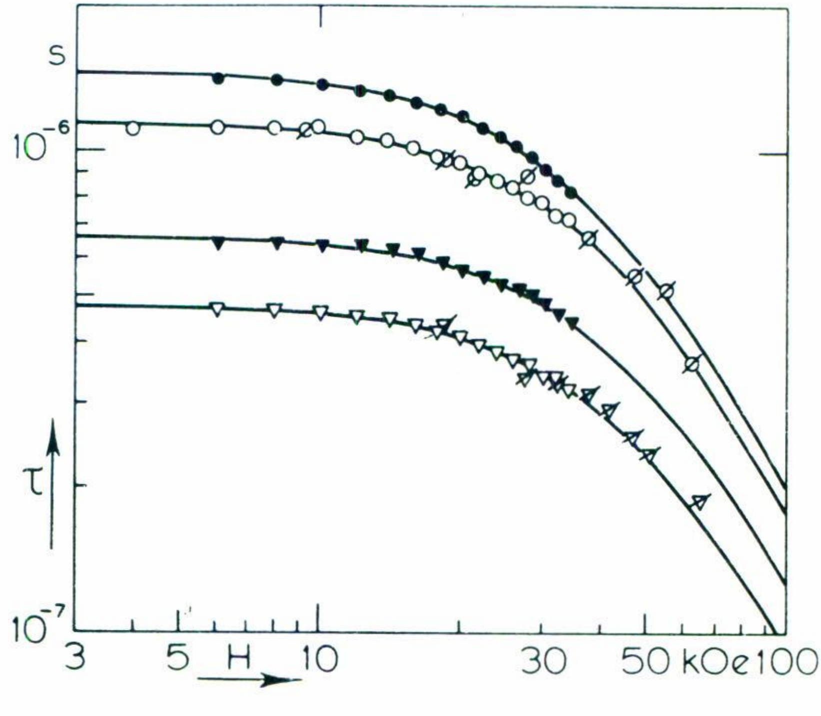

Fig. 9 Relaxation time versus external magnetic field at liquid hydrogen temperatures for $Co(NH_4)_2(SO_4)_2.6H_2O$ (closed symbols) and $CoK_2(SO_4)_2.6H_2O$ (open symbols)

○ : $T = 14.1$ K; ▽ : $T = 16.0$ K.

The measurements as described above do clearly demonstrate the occurrence of the various relaxation processes as predicted for isolated cobalt ions. The predictions for other Kramers ions such as Cu^{2+} and Yb^{3+} are similar. Recent experiments of De Vroomen[51] and Soeteman[52] show results identical to those given in figures 4 to 8.

II. RELAXATION PHENOMENA IN SOME MANGANESE AND CHROMIUM SALTS

A more complicated situation occurs if the ground state energy levels of the magnetic ion are not as simple as in the case of cobalt. If the next doublet is situated at an energy Δ so that $kT < \Delta < k\theta_D$ another relaxation mechanism may occur in addition to the terms given in eq. (1). This mechanism is possible due to the fact that the phonons can excite the magnetic spins into the next highest level. This so-called Orbach relaxation process[38] gives rise to an exponential temperature dependence of the relaxation time; an experimental verification can be found in[53].

The theoretical predictions change completely if $\Delta \ll kT$. In that case the theory of the direct process does not consider the relaxation due to transitions within one doublet, but to transitions between the various doublets. Such a process is more likely to occur and shows an H^2 instead of an H^4 dependence for τ^{-1}.[54] Also the T^9 Raman process changes; the straightforward calculation by putting the correct approximations in the general formulae for the transition probabilities leads to a T^5 Raman relaxation process[55]. The field dependent Raman relaxation has not been observed so far for Kramers ions of this group, thus it seems reasonable to describe the experiments by:

$$\tau^{-1} = \underset{\text{(direct process)}}{ATH^2} + \underset{\text{(Raman process)}}{BT^5 J_4(\theta_D/T)} \quad . \qquad (3)$$

Several hydrated salts with Mn^{2+} and Cr^{3+} ions do belong to the group of paramagnets with relaxation times that obey eq. (3). As early as 1947 Gorter gives in his book on paramagnetic relaxation[12] an impressive number of experimental results on various manganese and chromium salts. However, the limited range of temperatures and external magnetic fields did not allow a comparison with the 1947-version of eq. (3). In 1950 Bijl[56] measures temperature dependences for the relaxation times in manganese salts that are close to $\tau \propto T^{-5}$ but at that time the occurrence of the above mentioned Raman relaxation process was not yet understood theoretically. At present the experimental data of a whole series of manganese and chromium salts that obey eq. (3) are known, as an example we give the figures 10 and 11. In figure 10 one finds the relaxation times of $Mn(NH_4)_2(SO_4)_2.6H_2O$ (closed triangles, $H = 750$ Oe), and $MnSiF_6.6H_2O$ (open circles, $H = 1$ kOe). The ground states of both samples have to be described by three doublets with energy splittings of a few hundredths Kelvin. The relaxation times above 14 K clearly exhibit the T^5 Raman relaxation process with the change in slope of the log τ - log T graph due to the integral $J_4(\theta_D/T)$ at the higher temperatures.

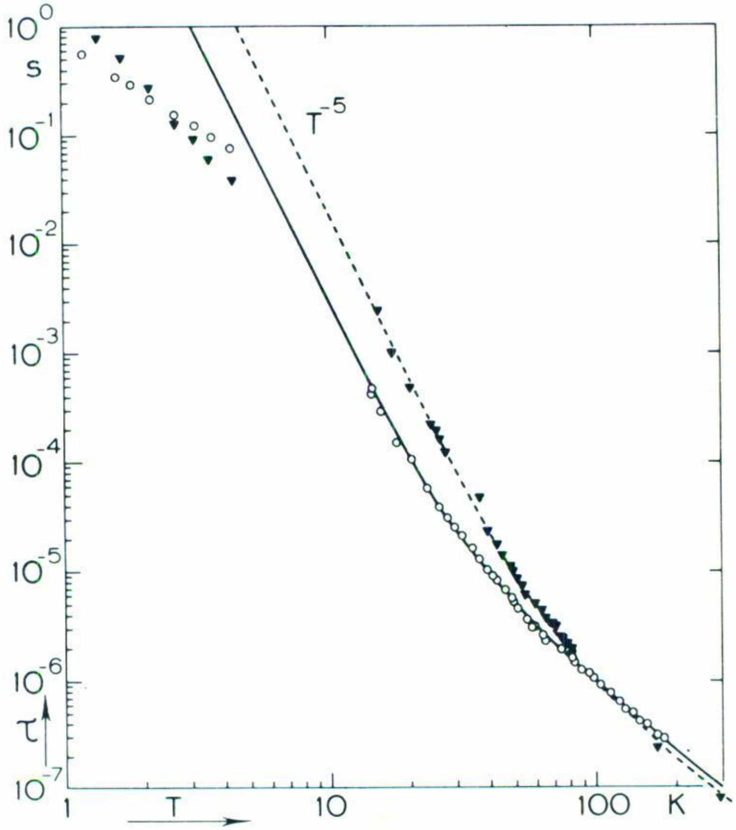

Fig. 10 Relaxation time versus temperature for powdered $MnSiF_6.6H_2O$ (○: $H = 1$ kOe) and $Mn(NH_4)_2(SO_4)_2.6H_2O$ (▼: $H = 750$ Oe)

At liquid helium temperatures the relaxation times of manganese samples become rather long. In such cases the results are highly sensitive to the occurrence of impurities (chemical or physical[41]). To observe the direct relaxation process one has to increase the external magnetic field as can be seen in figure 11. In this figure, where the spin-lattice relaxation times of manganese ammonium Tutton salt are shown, the curves $\tau \propto H^{-2}$ (drawn lines) are reached at approximately 10 kOe. One does not observe a large influence of phonon bottleneck effects as was the case for the systems described in section 3.2. The behaviour at weak fields is characteristic of that due to impurities[57]. At liquid hydrogen temperatures similar τ versus H curves are obtained. The dotted curves in figure 11 show the resultant τ versus H curve if at weak fields the Raman process (Brons–Van Vleck relation[39]) and at strong fields the direct process of eq. (3) is the effective relaxation mechanism. These lines agree nicely with the experimental results. Measurements as in figure 10 and 11 have been obtained for a number of salts. Some of the numerical results are given in table II.

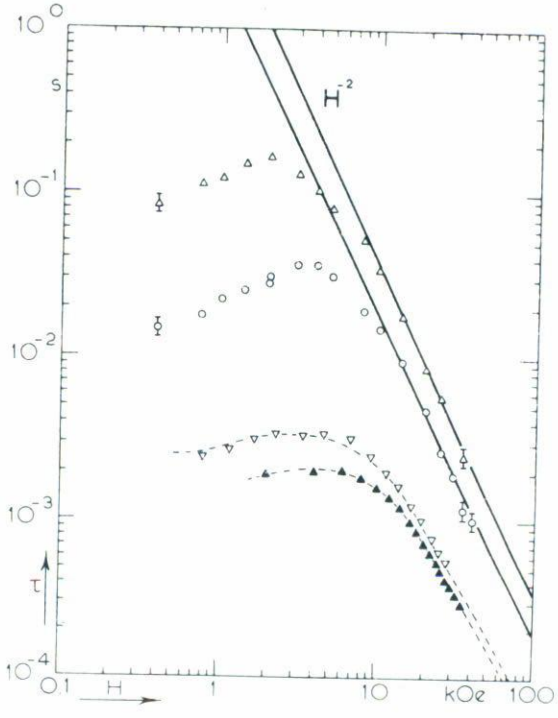

Fig. 11 Relaxation time versus external magnetic field for powdered $Mn(NH_4)_2.6H_2O$.
△: $T = 2.09$ K; ○: $T = 4.22$ K; ▽: $T = 14.2$ K; ▲: $T = 16.0$ K.
Lines are explained in the text.

TABLE II

Numerical results for the relaxation processes of eq. (3)

Sample	A^* ($s^{-1}K^{-1}kOe^{-2}$)	B($s^{-1}K^{-5}$)	θ_D(K)
$MnSiF_6.6H_2O$	0.2 – 0.3	0.75×10^{-4}	140
$Mn(NH_4)_2(SO_4)_2.6H_2O$	0.13 – 0.17	1.1×10^{-2}	280
$MnSO_4.4H_2O$	0.09 – 0.13	-	-
$CrCs(SO_4)_2.12H_2O$	0.9	2.3×10^{-4}	145
$Cr_{0.06}Al_{0.94}Cs(SO_4)_2.12H_2O$	2.4	2.3×10^{-4}	145

* as for table I

III. FINAL REMARKS

The examples given in sections I and II show that susceptibility measurements with a non-resonance technique lead to relaxation times that obey the predictions based on the theory for isolated paramagnetic ions. The above measurements are not the first verification of the theoretical predictions as resonance experiments had already shown the dependences in many cases, but these experiments are usually performed on magnetically diluted systems. The non-resonance experiments demonstrate that the situation is not much different for concentrated magnetic materials, although one has to increase the external magnetic field towards such values that the interactions with other relaxation possibilities can be neglected. The fact that this increase is possible is the great advantage of non-resonance techniques. Resonance experiments are usually restricted to one or a few frequencies and therefore the field dependence of the relaxation times cannot be studied. As long as the magnetic concentration is large enough, non-resonance experiments are possible for every value of the external magnetic field. This means that the sample has to contain at least 10^{17} spins ($S = \frac{1}{2}$) to obtain useful results at helium temperatures while for the modern resonance techniques only 10^{10} spins are needed.

The next thing to do in the study of paramagnetic relaxation is to bring the experimental and theoretical predictions into numerical agreement. For some ions of the iron group and for most rare earth ions this has been done successfully, although one has to take into account the order of magnitude character of the theoretical calculations. Minor differences as demonstrated by the values for A for instance in tables I and II, cannot be explained yet.

In the future we hope not only to extend our knowledge about the phenomena described in this paper, but also to perform detailed experimental studies of the paramagnetic relaxation in non-Kramers ions, which has not been considered so far. Other interesting phenomena to study will be the relaxation processes in the ordered (antiferromagnetic) state and near phase transitions[58].

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