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Abstract

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PARAMAGNETIC RELAXATION IN VANADYL SULFATE AND ITS SOLUTIONS

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Measurements of paramagnetic absorption were carried out in parallel fields of solid vanadyl sulfate $(VO)SO_4 \cdot 3.5H_2O$ and of its aqueous solutions at concentrations of 0.5, 1.5, 2.5, and 3.5 mole/liter. The measurements were performed by the Q-meter method (^{1}). Absorption curves were recorded as a function of the strength of the constant field H at four frequencies: 21, 21.5, 32, and 43 MHz. The spin-lattice relaxation times and the internal-field constants b/c were determined from measurements of χ' at two frequencies, assuming the validity of the Casimir–Du Pré equation with a correction for spin-spin absorption according to Shaposhnikov (^{1,2}).

Table 1

Values of $\rho_L \cdot 10^8$ (sec.) for solid vanadyl sulfate and its solutions

N, mole/l	H, oerst.	H, oerst.	H, oerst.	H, oerst.	H, oerst.	H, oerst.	H, oerst.
	1000	1330	1670	2000	2330	2670	3000
Powder	1.48	1.69	2.12	2.78	3.6	4.47	5.2
3.5	1.52	1.73	2.23	2.88	3.6	4.3	4.9
2.5	1.7	2.4	3.1	3.87	4.52	5.3	5.88
1.5	2.3	3.06	4	4.94	5.68	6.14	6.43
0.5	2.92	3.38	3.9	4.4	4.8	5.14	5.27

The values of ρ_L for solid vanadyl sulfate and its solutions, determined by the two-frequency method, are given in Table 1. The spin-lattice relaxation times, in addition to the two-frequency method, can also be determined from the graph of $\chi''(\nu)$. In Fig. 1a a plot is shown of the dependence of χ'' on frequency at a field strength $H = 2000$ oerst. The maximum absorption χ'' is observed under the condition that $\rho_L \nu \simeq 1$; from this the value of the spin-lattice relaxation time $\rho_L = 1/\nu$ can be determined.

It is seen from Fig. 1a that the curves $\chi''(\nu)$ have a maximum at approximately the same frequency both for the solid salt $(VO)SO_4$ and for its solutions. Hence

Fig. 1

Figure 1: Fig. 1

it should be expected that ρ_L in both cases will be of the order $1/\nu \simeq 10^{-8}$ sec. Indeed, the values of ρ_L, calculated by the two-frequency method both for solid vanadyl and for its solutions, are approximately equal to one another and have, at $H = 2000$ oerst, the values $2.78 \cdot 10^{-8}$ sec. for solid $(VO)SO_4 \cdot 3.5H_2O$, and for the solutions $\rho_L = 2.88 \cdot 10^{-8}$, $3.87 \cdot 10^{-8}$, and $4.94 \cdot 10^{-8}$ sec. at concentrations of 3.5, 2.5, and 1.5 mole/liter.

The spin-lattice relaxation times determined from the curves $\chi''(\nu)$ have, respectively, the following values: $2.86 \cdot 10^{-8}$, $2.86 \cdot 10^{-8}$, $3.3 \cdot 10^{-8}$, and $4 \cdot 10^{-8}$ sec.

If one takes into account that the curves $\chi''(\nu)$ were constructed from measurements of χ'' at only 4 frequency values ν, and, consequently, the position of the maximum was fixed with low accuracy, comparison of the numerical values of ρ_L determined by both methods indicates their sufficiently good agreement. This is an important confirmation of the correctness of the method for determining ρ_L from measurements of $\chi''(H)$ at 2 frequencies.

Let us dwell on the question of the reasons for the equality of the spin-lattice relaxation times in solid vanadyl and in its solutions. In itself this fact is somewhat unusual, since the experimentally found spin-lattice relaxation times in solid paramagnetic salts of other ions (for example, Mn^{2+}, Cr^{3+}) are at least an order of magnitude greater than the corresponding times in solutions. It is possible that the presence of strong exchange in solid vanadyl sulfate considerably shortens the spin-lattice relaxation time; whereas in solutions of this salt the exchange interactions, of course, exert a smaller influence on the relaxation. However, the shortening of ϱ_L in solid vanadyl sulfate as a result of exchange need not necessarily lead to equality of the spin-lattice relaxation times in the two states, so that from this point of view the observed agreement is purely accidental.

Fig. 1

On the other hand, the equality of the spin-lattice relaxation times might, it would seem, be explained by a peculiarity of the structure of the vanadyl salts themselves. The point is that $(VO)SO_4$ contains not simply the paramagnetic ion V^{4+}, but the molecular ion $(V \equiv O)^{2+}$, which has axial symmetry. Lloyd and Pake (³), considering the molecular ion of an inorganic free radical $ON(SO_3)_2^{2-}$, proposed that one of the sources of orbital-lattice interactions may be the natural vibrations of the molecular ion itself. If it is assumed that in our case as well the most effective source producing modulation of the local electric fields in both aggregate states is the natural vibrations of the molecular ion $(VO)^{2+}$, and that the system of Stark levels created by these local fields at the position of the V^{4+} ion is, as a rule, approximately analogous for both states, one may expect approximate equality of the spin-lattice relaxation times.

The dependence of the spin-lattice relaxation times on the strength of the constant field H_{11} is well described by the Bronson—Van Vleck formula ([4,5]).

The dependence of ϱ_L on the concentration N of $(VO)^{2+}$ ions in aqueous solutions of $(VO)SO_4$ is shown in Fig. 1b. It turned out that the spin-lattice relaxation time changes only slightly upon dilution; up to a concentration of ~ 1.5 mol/l, ϱ_L increases, while upon further dilution ϱ_L does not change within the experimental error. The lengthening of the spin-lattice relaxation time with dilution is apparently explained by structural changes occurring in the solution ([1,2]). On the other hand, the possibility is not excluded that at the very highest concentrations exchange interactions somewhat shorten ϱ_L.

The internal-field constant b/c changes very slowly with dilution and corresponds to a value $0.4 \cdot 10^{+6}$ Oe^2, whereas for solid $(VO)SO_4 \cdot 3.5H_2O$ $b/c = 0.95 \cdot 10^{+6}$ Oe^2.

The experimental data also make it possible to calculate the spin-spin relaxation times ϱ_s ([2]). Our calculations give a value of ϱ_s for solid sulfate

vanadyl $= 3.2 \cdot 10^{-9}$ sec, which is in fairly good agreement with the data of A. I. Rivkind ($\varrho_s = 1.9 \cdot 10^{-9}$ sec) ([6]). The graph of ϱ_s for aqueous $(VO)SO_4$ solutions as a function of concentration is shown in Fig. 1b. It is evident from the graph that ϱ_s increases rapidly upon dilution.

If the line width is calculated from the experimental values of ϱ_L and ϱ_s by the formula $\Delta H = 1/\varrho_L + 1/\varrho_s$ for the solid salt, we obtain $\Delta H = 178$ oersted, which is in very good agreement with the experimental value $\Delta H = 180$ oersted ([7]), obtained at a frequency $\nu = 10$ MHz. The ΔH calculated for the lowest concentrations in vanadyl solutions coincides with the width of an individual hyperfine component measured by the EPR method for the corresponding concentration ([8]).

Preliminary experiments carried out at frequencies of 3.2-12 MHz showed that there exists a second relaxation time, approximately 3 times longer than those given in Table 1. The existence of several spin-lattice relaxation times ϱ_L indicates the presence in the solution of systems with different environments around the paramagnetic ion $(VO)^{2+}$, which is consistent with the literature data ([9]) on complex formation in vanadyl solutions.

In conclusion, we take this opportunity to express our gratitude to B. M. Kozyrev for his guidance and constant assistance in the work, and to B. I. Kochelaev for participation in the discussion of the results.

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