MOTIONAL STATES OF PROTONS AND DIELECTRIC DISPERSION OF HEXAMMINE NICKEL CHLORIDE*

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Dielectric losses have been measured in hexammine nickel chloride crystals, which contain a system of protons (H^+ ions) that is responsible for a motional phase transition. The losses are well approximated by Debye curves, both above and below the transition temperature. Since this transition is not accompanied by the onset of a dipolar moment, long-range forces may be neglected, as in the similar but more complex case of hydrogen-bonded ferroelectrics, and the present results may shed light on the dynamical model of this class of substances.

A cooperative phase transition connected with the motional state of protons has been observed and investigated in hexammine nickel halides.[1-4] In these crystals ($NiCl_2 \cdot 6NH_3$ or other similar halides) the NH_3 groups occupy the vertices of regular octahedra disposed in a fcc array. The symmetry of the NH_3 groups does not fit the symmetry of the system. Therefore several equivalent configurations of minimum energy are available for the protons.[5] In this respect, these crystals are similar to hydrogen-bonded ferroelectrics,[6-10] ice,[11-14] and several biological substances,[15-16] and interesting phenomena can be expected in connection with the possibility of occurrence of collective motions of protons among different equivalent configurations.

ESR experiments have shown that the transition occurs with thermal hysteresis and isotopic effect.[2-4] The results are consistent with a model in which in the low-temperature phase, only collective rotational oscillations of the system of protons are allowed, while the high-temperature phase is characterized by uncorrelated rotations of the H_3 groups.[2-4] The collective motion of protons and the existence of dipolar moments of the NH_3 groups may be responsible for interesting dielectric properties of the system. Ferroelectricity was not expected to occur in view of the octahedral configuration of the NH_3 groups and of the probable permanence of a center of symmetry in the low-temperature phase. A possible tilting of the NH_3 groups relative to the octahedral axes, however, could conceivably be responsible for a resultant dipolar moment. A further possible point of interest in the transition observed in this type of crystal is the expected absence of long-range forces, which instead play a rôle in ferroelectric transitions.

We report here the results of experiments on the dielectric properties of $NiCl_2 \cdot 6NH_3$ and $NiCl_2 \cdot 6ND_3$ in powder form. The use of powders, instead of single crystals, is allowed by the fact, shown by already-published ESR experiments,[2-4] that the physical properties of these crystals are isotropic both above and below the transition. Furthermore, the large crystals needed for the present type of experiments would contain unwanted occlusions of the mother solution, which might greatly affect the results. The powders have been obtained by precipitation from the solution, which avoids strains introduced by grinding. The powder size changes with the precipitation rate, but it has no observable influence on the experimental results.

A Boonton 260 AP Q meter has been used in connection with a cryostat and with a continuous temperature control system[17] working from liquid helium to room temperature. The frequency was changed in steps, from 10^5 to 3×10^6 cps. The specimen filled a capacitor. This capacitor and a standard coil formed the resonant circuit whose Q value was measured. The parallel tuning capacitor, incorporated in the Q meter itself, was used to keep the resonance frequency constant when the temperature was changed.

Two loss curves are observed, respectively, above and below the transition. As shown in Figs. 1 and 2, these curves are well fitted by a Debye law:

$$\epsilon_r'' = (\epsilon_S - \epsilon_\infty)\frac{\omega\tau}{1+\omega^2\tau^2} \tag{1}$$

with a relaxation time given by

$$\frac{1}{\tau} = \frac{1}{\tau_0}\exp\left(-\frac{E}{KT}\right). \tag{2}$$

Since the losses occur in a small range of temperature, the data can be fitted equally well assuming for $\epsilon_S - \epsilon_\infty$ a constant value, or the tem-

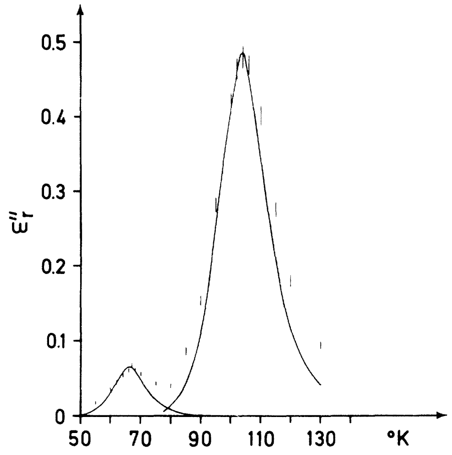

FIG. 1. Dielectric losses (ϵ_r'' vs T at 1 Mc/sec) in $NiCl_2$ hexammine. The continuous lines are calculated Debye laws fitting the experimental results.

perature-dependent expression

$$\epsilon_s - \epsilon_\infty = 4\pi N p_{\mathrm{eff}}^2/KT. \qquad (3)$$

The values of the parameters $1/\tau_0$, E, and p_{eff} used for the best fit of the experimental data with Eqs. (1)-(3) are given in Table I, together with the ϵ_r'' values at the maxima. If the frequency is chosen so that the loss curves overlap with the transition, ϵ_r'' jumps abruptly from the value relative to one Debye curve to that relative to the other when the transition temperature is reached. Hysteresis is observed if the temperature sweep is reversed. As shown by dc measurements, neither spontaneous polarization nor switching properties are present in the low-temperature phase.

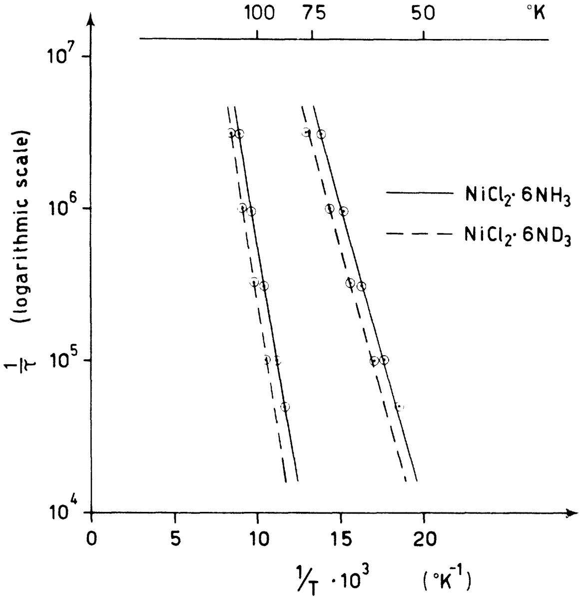

FIG. 2. Frequencies corresponding to the maxima of the ϵ_r'' Debye anomalies (i.e., reciprocal relaxation times) as a function of the reciprocal temperature, on a semilogarithmic scale.

At the transition temperature, an abrupt change in ϵ_r' is observed (Table I), from 6 ± 0.5 to 8.5 ± 0.5. This anomaly follows a hysteresis cycle, as do the other physical properties. Less conspicuous yet measurable variations of ϵ_r' are also observed in correspondence with the losses: In the high-temperature phase, the variation is about 0.8 ± 0.4, whereas in the low-temperature phase it is barely detectable. The large relative error is due to the fact that one is dealing with

Table I. Experimental values of ϵ_r' above and below the transition and of the parameters $\epsilon_{r\,\mathrm{max}}''$, $1/\tau_0$, and E as per Eq. (2) in the text. In the fourth column effective dipolar moments per NH_3 groups are given, as deduced from ϵ''. Here and in the text, ϵ_r' stands for ϵ'/ϵ_0 and ϵ_r'' for ϵ''/ϵ_0, where ϵ_0 is the dielectric constant of a vacuum.

	ϵ_r'	$(\epsilon_r'')_{\mathrm{max}}$	$10^{18} p_{\mathrm{eff}}$	$1/\tau_0$ (10^{12} cps)	E (°K)
$NiCl_2 \cdot 6NH_3$ ($T > T_c$)	6 ± 0.5	0.53 ± 0.05	0.29 ± 0.05	2 ± 0.4	1500 ± 20
$NiCl_2 \cdot 6ND_3$ ($T > T_c$)				2.4 ± 0.4	1620 ± 20
$NiCl_2 \cdot 6NH_3$ ($T < T_c$)	8.5 ± 0.5	0.078 ± 0.015	0.08 ± 0.02	0.9 ± 0.2	900 ± 20
$NiCl_2 \cdot 6ND_3$ ($T < T_c$)				0.4 ± 0.2	900 ± 20

small variations on a large background value. The measured order of magnitude of the ϵ_r' variations and of the $(\epsilon_r'')_{\max}$ values are quite consistent. Outside the temperature range in which the transition and the Debye curves are observed, a temperature dependence of ϵ_r' is not evident. These results consistently indicate that the polarization is due to several mechanisms, and only a small part of it is due to the mechanism which is responsible for the losses.

When the hydrogen is substituted by deuterium, the temperatures at which the losses occur are shifted. A Debye law is still obeyed, but with different values of the parameters (Fig. 2 and Table I).

This isotope effect and the fact that the two Debye curves, above and below the transition, are characterized by different values of the parameters indicate that the two phases correspond to different motional states of the proton system, with discontinuous and qualitative changes occurring through the transition. As the ESR results indicate,[1-4] in the high-temperature phase the H_3 groups are rotating independently from each other, whereas the low-temperature phase is characterized by collective rotational oscillations. The NH_3 dipoles can give a contribution to the dielectric properties through a tilting in different directions off the fourfold symmetry axes of the cubic structure. The above results indicate that different equilibrium configurations corresponding with this tilting are separated by potential barriers. The heights of the barriers are given by the E values in Eq. (2) and Table I. We interpret the relaxation process as a reorientation of this type occurring with the relaxation time given by Eq. (2) and through the mentioned barriers among these different configurations. By comparison of the experimental values with the dipole moment of the free NH_3 molecules (1.47×10^{-18} cgs), it can be concluded that tilt angles of at most a few degrees are permitted and even smaller tilt angles occur in the low temperature phase.

The isotopic effect in τ_0 observed in the low-temperature phase is conspicuously larger than that observed above the transition (see Table I). This points out that a motion involving only (or essentially) hydrogen atoms is relevant below the transition. Therefore the only potential barriers involved are those acting on the H_3 (or D_3) groups. In the high-T region, the τ_0 values are not significantly changed by the same substitution, pointing out that the dynamics of the crystals as a whole is also involved in the process. This also agrees with the larger values observed for the barrier heights.

In conclusion, we believe that the situation observed here is in some respects similar to that of hydrogen-bonded ferroelectrics. However, the present case is simpler in the sense that a ferroelectric ordering does not occur here, and long-range forces may therefore be neglected. A further similarity is due to the fact that a Debye model does apply (approximately) to the mentioned class of ferroelectrics.[10-19] These circumstances make a further investigation of the present case useful for a simplified approach to the study of the dynamical behavior of hydrogen-bonded ferroelectrics (including ice), for which a description in terms of the Cochran-Fröhlich model[10-18] is not as satisfactory as for the $BaTiO_3$ class. The inapplicability of a "soft-mode" model to hydrogen-bonded ferroelectrics is suggested by analogy with the present case in which the proton system in the high-temperature phase may behave like a fluid (at least with respect to some appropriate degrees of freedom) rather than like a solid possessing definite phonon modes.

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SPIN-LATTICE RELAXATION OF V^{4+} PARAMAGNETIC IMPURITIES IN TiO_2[†]

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The electron spin-echo technique has been used to measure the spin-lattice relaxation of V^{4+} paramagnetic impurities in rutile (TiO_2) at liquid-helium temperatures. The relaxation of the z component of magnetization shows a time dependence, the sum of two exponentials with two time constants T_{1a} and T_{1b}. In the liquid-helium temperature range, both time constants are independent of temperature. The relaxation times are independent of sample size and surface condition but are dependent on annealing history. The results of this study suggest that T_{1b} is related to the phonon relaxation time due to crystal-defect scattering.

Recent experiments in EPR indicate that the process of spin-lattice relaxation for the iron-group impurities in single-crystal insulators is more complicated than the theory of Van Vleck[1] indicates. The purpose of this Letter is to present some experimental results of our study of the spin-lattice relaxation of V^{4+} paramagnetic impurities in a single crystal of TiO_2 (rutile). The measurements were made at liquid-helium temperatures from 1.3 to 4.2°K and with a V^{4+} impurity concentration of about 0.05%.

The spin-lattice relaxation time T_1 was measured using an electron spin-echo[2] spectrometer operating at about 9 Gc/sec with a pulse power of about 1 kW. The microwave pulse sequence is shown in Fig. 1. Four pulses (two pulse pairs), with pulse widths of about 30 nsec, are applied to the spin system. The first pulse pair, a θ pulse and a 180° pulse separated by a time τ, produce an echo with an amplitude A_0 which is proportional to $\sin\theta$ times $M_z(0)$, the magnetization along the z axis at time zero. After a time t, a second pulse pair, equivalent to the first pulse pair, is applied to the system and produces an echo with an amplitude A_1 which is proportional to $\sin\theta$ times the magnetization along the z axis at time t. In our experiments, the time τ was about 3 μsec and was held fixed. The time t

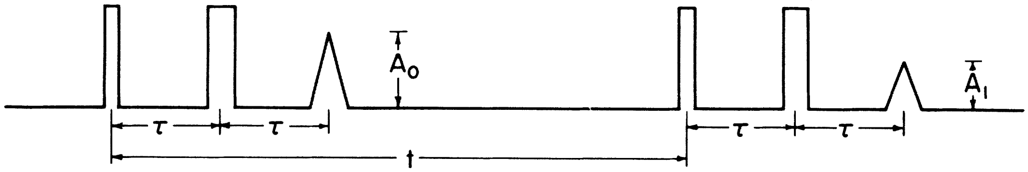

FIG. 1. Four-pulse spin-echo pulse sequence for the measurement of T_1. The θ pulse rotates the z component of magnetization away from the z axis by an angle θ. The 180° pulse rotates the magnetization by 180° to produce an echo A_0 or A_1. The separation between the pulses τ is fixed at 3 μsec. The time t between pulse pairs is varied from 5 msec to 1.2 sec.