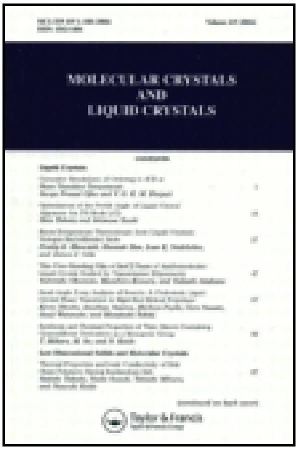

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

Spin Lattice Relaxation Time Measurements on Cholesterol Derivatives

D. Cutler [a]

[a] Department of Physics, University of North Carolina, Chapel Hill, North Carolina

Version of record first published: 28 Mar 2007.

To cite this article: D. Cutler (1969): Spin Lattice Relaxation Time Measurements on Cholesterol Derivatives, Molecular Crystals, 8:1, 85-92

To link to this article: http://dx.doi.org/10.1080/15421406908084899

Molecular Crystals and Liquid Crystals. 1969. Vol. 8, pp. 85–92

Printed in Great Britain

Spin Lattice Relaxation Time Measurements on Cholesterol Derivatives

D. CUTLER

Department of Physics
University of North Carolina
Chapel Hill, North Carolina

Abstract—We have used a N.M.R. pulse apparatus operating at 10 MHz to measure the variation of T_1, the spin-lattice relaxation time, with temperature for some cholesterol esters. Measurements were made from 25 °C to 120 °C.

Distinct changes in T_1 have been observed at temperatures which also show changes in the optical properties. Over some temperature ranges a nonexponential relaxation process has been found which is interpreted as indicating the presence of two distinct types of motion.

Introduction

The effects of molecular motion on the spin-lattice relaxation time, T_1 were first described by Bloembergen, Purcell, and Pound, in 1948.[1] Since then this N.M.R. technique has proved to be a useful tool for the measurement of molecular motion and activation energies for this motion in some materials. In 1950 the pulse method for measuring T_1 was described by Hahn,[2] which simplifies the measurement of this parameter.

Theory

It can be shown that for a material containing protons placed in a magnetic field H_0 and subject to a series of 90° pulses that:

$$M_t = M_\infty\left(1 - \exp - \frac{\tau}{T_1}\right)$$

Where:

τ = Spacing between the 90° pulses.

M_τ = Magnetization following a 90° pulse.

M_∞ = Magnetization for a pulse spacing much greater than T_1.

Now for a material in which there is molecular motion we find that:

$$\frac{1}{T_1} \approx \text{Const}\left(\frac{\tau_c}{1+\omega_0^2\tau_c^2}\right)$$

Where:

ω_0 = Resonant frequency in the mangetic field H_0.

τ_c = Correlation time for the molecular motion.

τ_c is related to the activation energy through the usual relation:

$$\frac{1}{\tau_c} = \frac{1}{\tau_0}\exp - \frac{E_D}{RT}$$

Where:

τ_c = Correlation time at absolute temperature T.

E_D = Activation energy for the motion.

So far we have only considered a simple system, however if there is more than one type of motion we should write:

$$M_T = M_{1\infty}\left(1 - \exp - \frac{\tau}{T_{11}}\right) + M_{2\infty}\left(1 - \exp - \frac{\tau}{T_{12}}\right) + \ldots$$

i.e. we will find a nonexponential recovery of M_0 from which we may obtain a number of T_1's.

Results

We have measured T_1 for cholesteryl nonanoate and cholesteryl butyrate from room temperature to about 120 °C.

Cholesteryl Nonanoate

In Fig. 1 we show the fractional magnetization as a function of τ using an inverted log. scale for cholesteryl nonanoate at 105 °C. We see a nonexponential recovery which we take to be the sum of two exponentials, the intercept, I, giving the fraction of protons contributing to the short T_1.

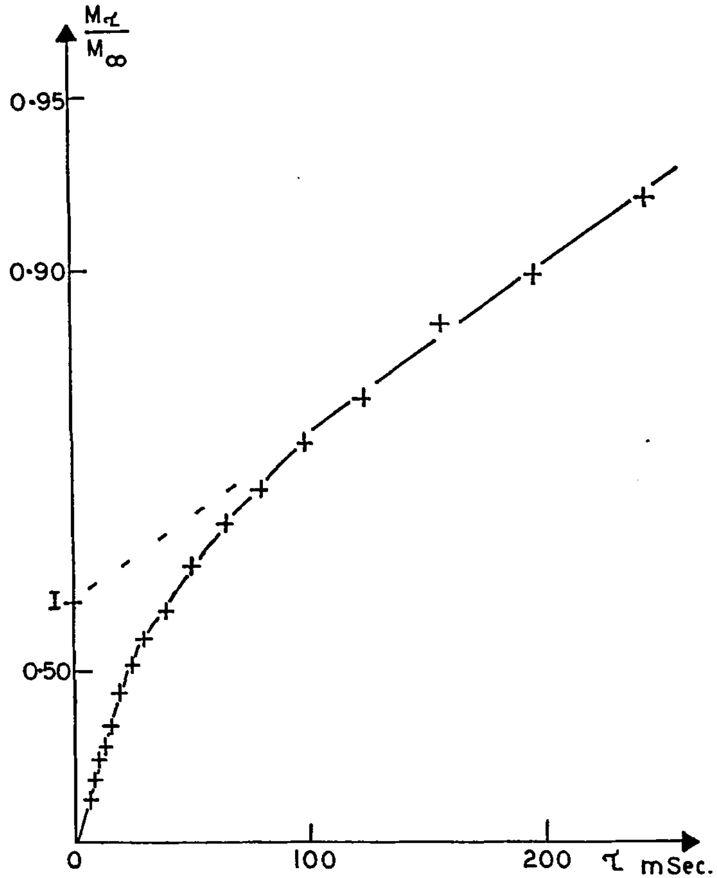

Figure 1. Recovery of magnetization as a function of τ for cholesteryl nonanoate at 105 °C.

In Fig. 2 we show the variation of T_1 with temperature for cholesteryl nonanoate. This material is a solid at room temperature and we were not able to make measurements below 70 °C because of the short T_2. Up to 85 °C we observe a single T_1 with a minimum, indicating considerable motion in the solid. Using

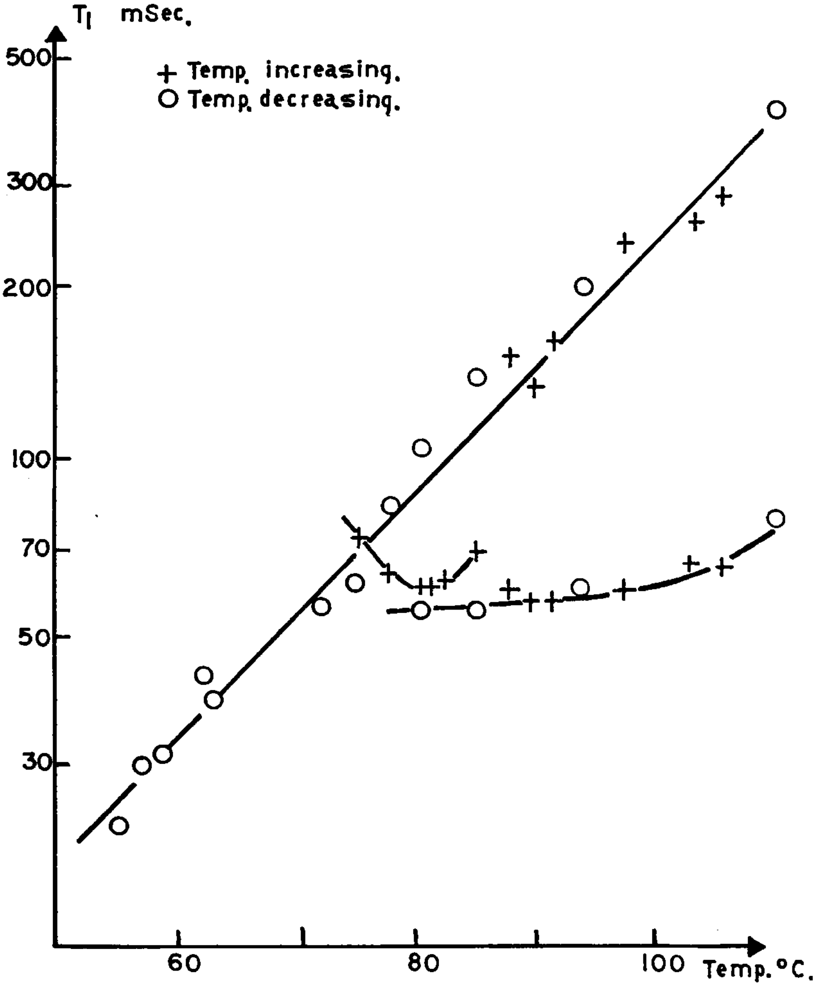

Figure 2. Variation of T_1 with temperature for cholesteryl nonanoate.

the relation $\omega_0^2\tau_c^2 = 1$ at the minimum, and substituting our value of $\omega_0 = 2\pi \times 10^7$, we find $\tau_c \approx 1.6 \times 10^{-8}$ sec. at 81 °C. Above 85 °C we observe two T_1's. We believe that a phase transition occurs near this temperature. Unfortunately because of the construction of the N.M.R. probe it was not possible to observe the sample to confirm this, however other optical measurements show a phase transition to the isotropic liquid at just below 90 °C. for this sample. This is a somewhat lower temperature than that reported by Gray,[3] who gives 92 °C. The difference is possibly due to impurities in the sample. On reducing the temperature we find that the two T_1's remain until 80 °C after which we find only a single T_1 to 55 °C when T_2 again becomes too short for our apparatus. Gray[3] gives 80.5 °C and 77.5 °C for the two mesophase transitions in this material. Again because

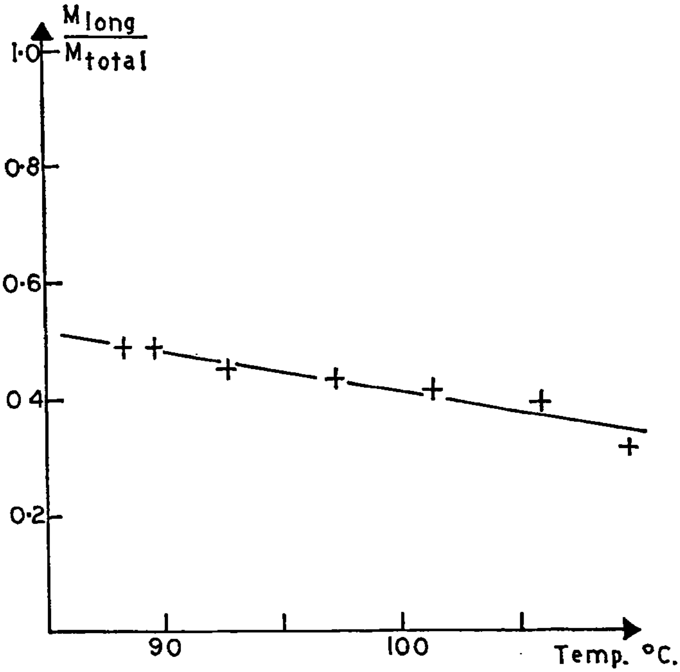

Figure 3. Fraction of protons contributing to the longer T_1 as a function of temperature for cholesteryl nonanoate.

of the construction of our apparatus we cannot say at which mesophase transition we observe this change, but we can say that there is a single T_1 in the low temperature mesophase and that this appears to be a continuation of the longer T_1 in the isotropic liquid. If we calculate an activation energy for the molecular motion giving this T_1 we find that: $E_D \approx 12.5$ Kcal/mol.

In Fig. 3 we show the fraction of protons contributing to the longer T_1.

CHOLESTERYL BUTYRATE

The variation of T_1 with temperature for cholesteryl butyrate is shown in Fig. 4. This material also shows a nonexponential relaxation at the higher temperatures changing to a single relaxation below 98 °C, again near the value of 102 °C given by Gray[3] for the transition to the mesophase. We have also calculated the activation energy for the longer T_1 in this sample and obtain $E_D \approx 11.0$ Kcal/mol. The fraction of the protons contributing to the longer of the two T_1's was found to be very similar to the case of the nonanoate.

Conclusions

We have observed two T_1's in the isotropic liquid phase for both the materials studied which changes to a single relaxation at the transition to the mesophase. With the limited amount of data it is not possible to give the cause of these two relaxation processes. It is possible that they arise from some form of molecular aggregation in the isotropic liquid, which would agree with some observations by Cameron.[4] The values observed for the activation energy for the motion common to both the isotropic liquid and the mesophase are very similar to those given by Porter and Salamoto[5] for other cholesterol esters from viscosity measurements.

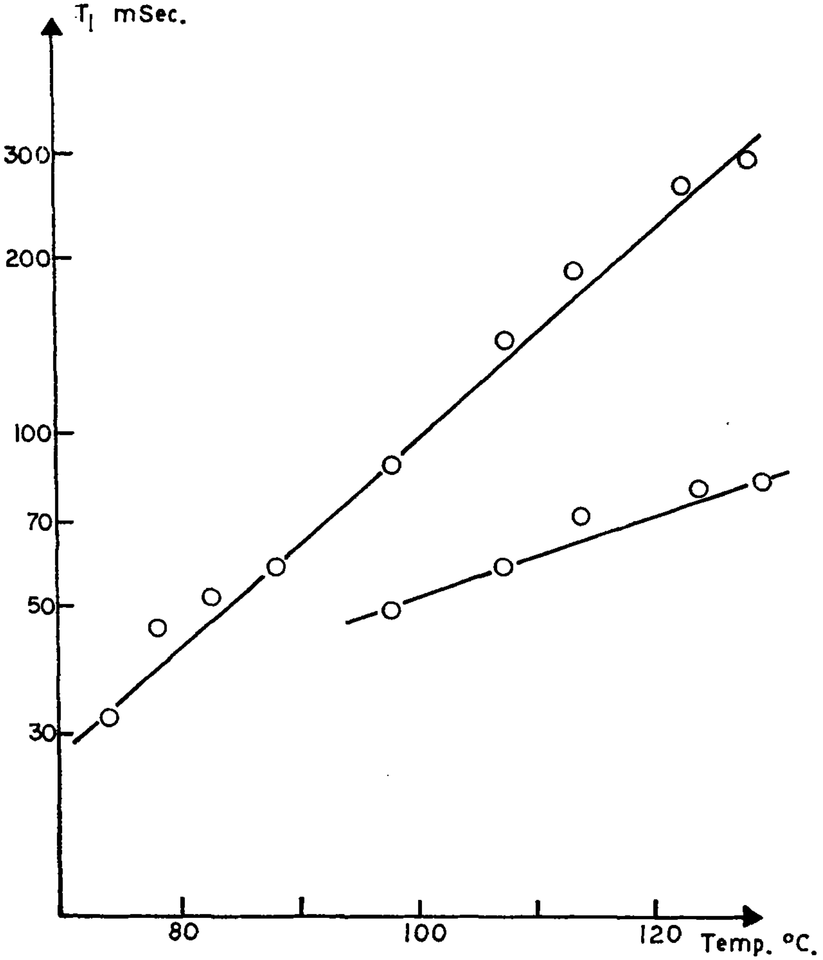

Figure 4. Variation of T_1 with temperature for cholesteryl butyrate.

Acknowledgments

We wish to thank Dr. G. T. Stewart for the samples, optical observations of the phase transitions, and many helpful discussions during the course of this work.

This research was carried out under a grant from the Advanced Research Projects Agency.

REFERENCES

1. Bloembergen, N., Purcell, E. M. and Pound, R. V., *Phys. Rev.* **73**, 679 (1948).
2. Hahn, E. L., *Phys. Rev.* **80**, 580 (1950).
3. Gray, G. W., *J. Chem. Soc.* 3733 (1956).
4. Cameron, L. M., Second International Liquid Crystal Conference (1968).
5. Porter, R. S. and Salamoto, K., Second International Liquid Crystal Conference (1968).