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Proton spin–lattice relaxation in meta-carborane

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In a recent work, the temperature dependence of the proton spin–lattice relaxation time $T_1$, was investigated in ortho- and para-carborane between 170 and 310 K and between 210 and 320 K, respectively. We have completed the present phase of the study by measuring $T_1$ at 30 MHz in meta-carborane between 171 and 303 K. The experimental technique is discussed in Ref. 1 and schematic diagrams of the three isomers of carborane can also be found in Ref. 1.

The experimental results for meta-carborane are shown in Fig. 1. There is a first order phase transition at about 276 K. The dashed curve below 220 K ($10^{13} T^{-1} > 4.5$) in Fig. 1, shows a linear least squares fit of the data in this region and yields an activation energy of 25 kJ/mol. The region on the high temperature side of the $T_1$ minimum in the low temperature phase cannot be fitted to a straight line because the transition occurs before the short correlation time limit in the low temperature phase is reached. We show a dashed line corresponding to an activation energy of 40 kJ/mol in order to compare the results in meta-carborane with those of the other two isomers (Table II of Ref. 1).

The details in the vicinity of the phase transition are shown in Fig. 2. Nonexponential relaxation is indicated by vertical dashed lines and is indicative of both phases being present. (This is discussed more fully in the previous work.) Although only the short time $T_1$ or the long time $T_2$ was measured in most cases, for three runs both time constants were measured and these are indicated by pairs of data points connected by the vertical dashed lines. The lengths of the other five vertical dashed lines in Fig. 2 have no significance. Taking the transition temperature as the midpoint of the coexistence range, on increasing the temperature, the transition oc-

FIG. 1. Spin–lattice relaxation time $T_1$ vs temperature $T$ in meta-carborane. The experimental results are indicated by closed circles and the dashed lines are discussed in the text. The details in the region of the phase transition are shown in Fig. 2.
FIG. 2. Spin-lattice relaxation time $T_1$ vs temperature $T$ in the vicinity of the phase transition in meta-carborane. Note that one decade is omitted on the abscissa between the $T_1$ values in the two phases. The circles and triangles denote decreasing and increasing temperature, respectively. The vertical dashed lines indicate nonexponential relaxation which is discussed further in the text.

curs at 279.3 ± 2.8 K and on decreasing the temperature it occurs at 272.5 ± 3.9 K. The coexistence ranges are 5.5 ± 2.3 K and 10.9 ± 3.4 K on increasing and decreasing the temperature, respectively, and the hysteresis range is 6.8 ± 5.7 K. The origin of the uncertainties is discussed in the previous work.1 These temperatures for meta-carborane can be compared with those for the ortho and para isomers (Table I in Ref. 1).

The temperature dependence of $T_1$ in the three isomers of carborane is summarized in Fig. 3. The ortho1 and meta isomers undergo one phase transition in the temperature region studied whereas the para isomer1 undergoes two transitions. The present experiments in meta-carborane tend to support the conjectures put forth in the previous work1 in that the high temperature phase transition in meta-carborane occurs at a temperature between that found for the other two isomers and at low temperatures, meta-carborane behaves like ortho-carborane and not like para-carborane, particularly with respect to the lack of a second phase transition. The origin of the difference between the $T_1$ vs $T$ curves for ortho- and para-carborane is discussed in detail in the previous work1 and is based on the fact that the ortho (and meta) isomers have a relatively large molecular electric dipole moment whereas para-carborane has none.

There are important problems which still require investigation in the carborane system and these are discussed in the previous work.1

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Spin-orbit coupling and $A$-doubling in LiO

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Theoretical calculations of molecular spectroscopic properties have reached a stage where in some instances they challenge experimental determinations. This is true even in the accurate radio frequency region since parameters are derived by fitting observed transitions using formulas which necessitate assumptions about