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Abstract

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PHASE TRANSITIONS AND CHANGES IN THE STRUCTURE OF NUCLEAR MAGNETIC RESONANCE LINES IN BERYLLIUM OXYACETATE

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To clarify the nature of the phase transitions and the mechanism of interaction between individual methyl groups, the dependence of the shape and moments of the NMR line on temperature was investigated in a polycrystalline sample of beryllium oxyacetate, $Be_4O(COOCH_3)_6$. Beryllium oxyacetate has second-order phase transitions at temperatures of 42, 77, and 124°. The existence of these transitions was detected from the temperature dependence of the coefficient of thermal expansion (1) and by direct measurements of the heat capacity (2). At a temperature of 32°, the value of the coefficient of thermal expansion changes sharply; however, the dependence of the heat capacity on temperature remains monotonic. At a temperature of 148° a first-order phase transition occurs, which is also confirmed by X-ray structural studies. At temperatures above 160° the beryllium oxyacetate crystal gradually passes into the state of a "plastic crystal" and melts at a temperature of 286.7° (3).

We recorded the NMR absorption line using apparatus described earlier (4). The amplitude of the high-frequency field was chosen such that there was no saturation in the sample over the entire temperature range studied. The mean error of an individual measurement of the second moment was no more than 2%, and of the fourth, no more than 6%. The combined effect of the time constant of the recording device and the finite modulation amplitude on the measured values of the moments was taken into account by means of ratios (5). The studies were carried out in the range 20–200°, with the thermostatting accuracy not worse than $\pm 0.1^\circ$.

Our measurements showed the absence of any changes in the line shape and its moments in the temperature interval from 20 to 135°. However, the line shape proves to be unchanged only for equilibrium states. When the temperature range is traversed rapidly near the temperatures at which a sharp change in the coefficient of thermal expansion occurs (a second-order phase transition), a strong change in the magnitude of the second moment occurs. Far from these temperatures, the phenomenon is not observed. Figure 1 shows the dependence

Figure 1

Figure 1: Figure 1

of the second moment on temperature for beryllium oxyacetate in the temperature interval 20-60° for different thermostatting times. It is evident from the figure that, as the thermostatting time increases, the dependence of the magnitude of the second moment on temperature decreases. If, before measuring each point, the sample was thermostatted for 3 hours, the second moment proved to be unchanged. The dependence of the magnitude of the second moment on time near the temperature of the sharp change in the coefficient of thermal expansion was also measured. For this purpose, after changing the sample temperature from 31.0 to 32.0°, successive measurements of the second moment of the line were made at intervals of 30 min.

The value of the second moment underwent damped oscillations with time about the equilibrium value. The maximum amplitude of deviation from the equilibrium value was +1.0 gauss^2, with an accuracy of measurement of the second moment in this series of measurements of 0.20 gauss^2. The period of the oscillations was $\sim$ 1 h. After $\sim$ 3 h the value of the second moment, within the accuracy of the experiment, became equal to the equilibrium value.

Fig. 1. Time required to establish equilibrium: *a*—30 min, *b*—90 min

The observed effect is apparently associated with a change in the rate and character of the motion of individual molecules and their elements (in our case, CH_3 groups) in the absence of thermodynamic equilibrium near temperatures at which a rapid change in the coefficient of thermal expansion occurs (a second-order phase transition). Indirect confirmation of the generality of this effect may be provided by the existence of a scatter in the values of the second moment near the points of a second-order phase transition, which can be observed in the work of some authors (for example, (^{6})). Further results of the study of this effect (including on a single crystal) will be published.

In stationary measurements the second moment of the NMR line of beryllium oxyacetate in the temperature range 20—135° is equal to 6.90 ± 0.10 gauss^2. The ratio of the fourth moment to the square of the second is 3.30. The experimentally obtained derivative function of the line shape (one half of it) is shown in Fig. 2A (curve 1). The value of the second moment of the NMR line for beryllium oxyacetate at room temperature was also calculated. In the calculations, the interatomic distances and the parameters of the crystal lattice given in Ref. (^{7}) were used. The value of the second moment, calculated for the powdered sample by means of the formulas of Andrew and Eades (^{8}) under the assumption that the methyl groups reorient about a sixth-order axis perpendicular to the plane in which the hydrogens lie, is 6.85 gauss^2. In the calculations the interaction of the protons of methyl groups only with the four nearest methyl groups belonging to different molecules was taken into account. An estimate

Figure 2

Figure 2: Figure 2

of the contribution to the second moment made by interaction with beryllium nuclei and with the protons of the remaining methyl groups gives a value of 0.02 gauss^2. The obtained

Fig. 2. A—$\beta/\alpha = 0.36$; B—$\beta/\alpha = 0.26$. 1—experimental curves, 2—theoretical curves

the value of the second moment coincides, within the accuracy of the experiment, with the measured one.

At temperatures above 150°, after the first-order phase transition, another maximum appears on the curve of the derivative of the line-shape function (Fig. 2B, curve 1). The second moment decreases and becomes equal to 6.20 gauss^2. The ratio of the fourth moment to the square of the second increases to 3.50. The half-width of the line at the first maximum decreases somewhat in comparison with the half-width at room temperature. The half-width at the second maximum proves to be equal to the distance between the lines in the spectrum of the methyl group (3.7 gauss). With a further increase of temperature to 200°, the shape and moments of the line do not change.

The appearance of line structure and the decrease in the value of the second moment after the first-order phase transition can easily be explained by a decrease in the interaction between the magnetic moments of protons belonging to different molecules, owing to an increase in the distance between them. The spectrum of a rotating methyl group consists of three lines. These lines are broadened owing to intermolecular interaction. With an accuracy sufficient for a qualitative consideration, it may be assumed that the intermolecular interaction leads to a Gaussian shape for each of the lines of the spectrum. The derivative of the line-shape function calculated in this approximation is shown in Figs. 2A and 2B (line 2). The parameter β, which determines the half-width of the Gaussian distribution of each of the spectral components, was chosen equal to that measured experimentally from the magnitude of the second moment for the high-temperature (B) and low-temperature (A) modifications of beryllium oxyacetate. The experimental value of β is determined from the known relation $M_2 = \frac{2}{5}\alpha^2 + \beta^2$, where α is the distance between the lines in the spectrum of the methyl group; M_2 is the measured value of the second moment. The qualitative agreement with experiment is satisfactory. It should be noted that the second maxima on the curves of the derivative of the line-shape function appear at $\beta/\alpha < 0.3$, which corresponds to the experiment, including that of other authors.

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Note: Figure translations are in progress. See original paper for figures.