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^{35}Cl spin-lattice relaxation study of phase transitions in CsPbCl$_3$[†]

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Nuclear-spin–lattice relaxation-time measurements of the chlorine nuclei in the perovskite compound CsPbCl$_3$ are reported for the temperature range from 112 to 360 K. The data show a discontinuity at 320 K, that is, at the highest-temperature phase transition. The behavior of the relaxation data in the cubic phase is as expected for a highly anharmonic crystal; the behavior in the distorted phases reflects the softening of the zone-boundary rotary-mode phonons which drive the phase transition.

INTRODUCTION

Many cubic perovskite crystals undergo phase transitions in which they transform to slightly distorted structures from the ideal perovskite-type structures. It is well established[1] that these phase transitions are caused by the condensation of the particular normal modes of the phonon in the cubic phase whose eigenvectors relate to the atomic displacements in the stabilized structure below the transition temperature T_c. The frequency of this phonon mode decreases as the temperature is lowered to T_c, and at T_c, the restoring force for this mode vanishes, allowing the atoms to shift to new equilibrium positions.

The perovskite crystal CsPbCl$_3$ has recently become the subject of considerable interest. A phase transition at 320 K was first observed in 1959 by Møller.[2] He carried out a structural analysis and reported that the basic structure of the crystal was of the perovskite type. In 1969 Sakudo *et al.*[3] reported the results of an x-ray-diffraction study, Hirotsu and Sawada[4] provided optical data, Tovborg-Jensen[5] performed nuclear-quadrupole-resonance measurements, and Cape *et al.*[6] carried out EPR studies. These measurements confirmed the existence of three phase transitions at 320, 315, and 310 K. In 1970 and 1971, Hirotsu[7] made extensive experimental studies including dielectric constant, elastic constant, specific heat, optical, and Raman-scattering measurements. In 1974 neutron scattering data[8] elucidated the mechanism of these phase transitions and showed that they are associated with the condensation of rotational modes of PbCl$_6$ octahedra around the three principal axes. This interpretation is confirmed by x-ray[9] and electron-diffraction data.[10]

The purpose of the present paper is to report on a ^{35}Cl spin-lattice-relation investigation of CsPbCl$_3$ and to show that the results are consistent with the picture that has emerged from the neutron scattering study.

RELAXATION DATA AND THEIR INTERPRETATION

The ^{35}Cl spin-lattice-relaxation times (T_1) in a powder sample of CsPbCl$_3$ were measured in a pure nuclear-quadrupole-resonance (NQR) experiment for the temperature range 112–360 K. A phase coherent pulsed magnetic resonance spectrometer of conventional design was used in either a two or three pulse configuration to obtain the data. The sample was purchased from Atomergic Chemetals and used as received.

Figure 1 shows the relaxation times deduced. Below 320 K, the values of T_1 associated with the high- and low-frequency resonances reported by Tovborg-Jensen[5] are indicated by different symbols. Within the experimental uncertainty of ± 5%,

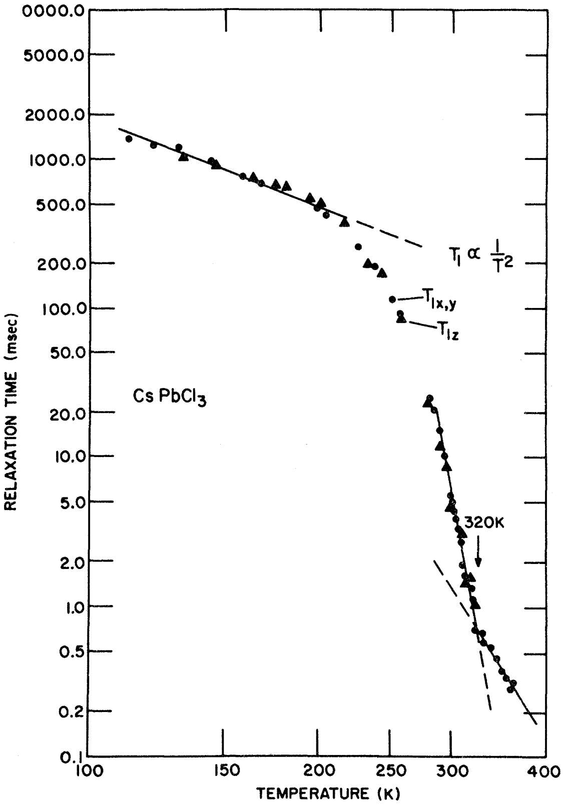

FIG. 1. Temperature dependence of the ^{35}Cl spin-lattice-relaxation time in CsPbCl$_3$.

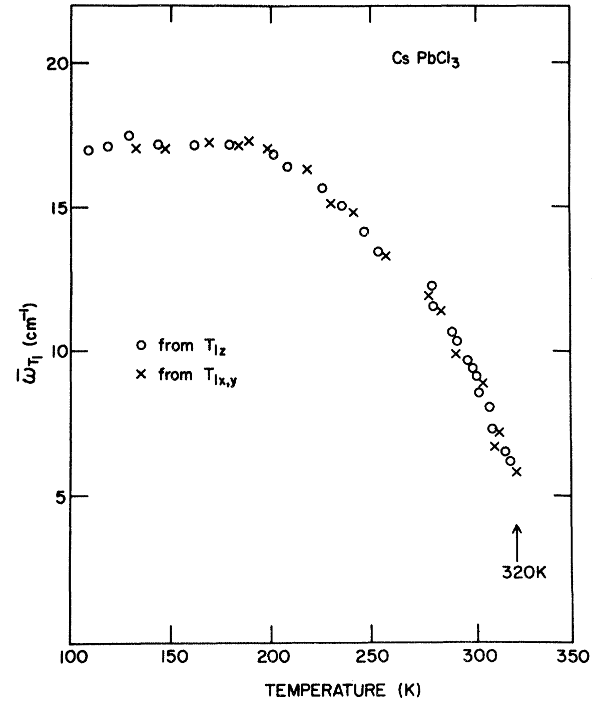

FIG. 2. Temperature dependence of the Brillouin-zone averaged rotary-mode frequency $\bar{\omega}_{T_1}$ in CsPbCl$_3$, as deduced from the ^{35}Cl spin-lattice relaxation-time data.

both sets of relaxation-time data are coincident. From the graph it is seen that T_1 spans almost four orders of magnitude ranging from ~ 1.5 sec at 112 K to ~ 0.3 msec at 360 K. The occurrence of a discontinuity in the temperature dependence of T_1 at 320 K coincides with the discontinuity in the behavior of the NQR frequency at the same temperature that indicates the high-temperature phase transition. However, from the T_1 data there is no evidence of the other phase transitions at 310 and 315 K.

It is instructive to compare these data in CsPbCl$_3$ with the ^{79}Br relaxation-time data reported[11] for K$_2$PtBr$_6$, a compound possessing the cubic antifluorite structure at high temperatures. The cubic perovskite (RMX_3) and cubic antifluorite (R_2MX_6) structures are very similar, both being describable in terms of a framework of MX_6 octahedra with the R ions occupying interstitial sites. The NQR frequency data in K$_2$PtBr$_6$ indicate phase transitions at 169, 143, 137, 105, and 78 K. Although the T_1 data strongly reflect the occurrence of the phase transition at 169 K, these data provide no evidence of the transitions at lower temperatures. In this sense, the ^{35}Cl T_1 data for CsPbCl$_3$ are similar to the ^{79}Br T_1 data for K$_2$PtBr$_6$. However, the ^{79}Br T_1 data exhibit a pronounced minimum coinciding with the highest-temperature phase transition, whereas the ^{35}Cl T_1 data do not. In this regard, the CsPbCl$_3$ data are anomalous. The observation of relaxation-time minima associated with structural phase transitions has been reported in a large number of compounds including many RMO_3 pervoskites.[12] Unlike the other substances, however, CsPbCl$_3$ is known to be very anharmonic near 320 K. Hirotsu[7] determined the temperature dependence of the soft-mode frequencies by Raman-scattering experiments in the distorted phases and noted that the soft modes become heavily damped above 300 K. This observation has been verified and its range of applicability extended to 353 K by means of the neutron scattering experiments of Fujii *et al.*[8] These data show that the Debye-Waller factor for the chlorine ions is extraordinarily large in the cubic phase. This result suggests that the PbCl$_6$ octahedra may be able to undergo hindered rotational motions above 320 K. The occurrence of such motions would provide a very efficient second relaxation mechanism for the chlorine nuclear spins, which would give an extra contribution to the nuclear-spin-relaxation rate of the form[13]

$$T_1^{-1} = Ce^{-V_0/kT} ,$$

where C is a constant and V_0 is the height of the potential barrier to rotation. As a result, the observed T_1 would continue to decrease as the temperature increased above 320 K.

Below 300 K, where the lattice anharmonicity is greatly reduced, a perturbation treatment of the anharmonic contribution to nuclear-spin relaxation[14] should apply. In this case, the relaxation rate is given by

$$T_1^{-1} = CT^2/\bar{\omega}_{T_1}^5 ,$$

where T is the temperature and $\bar{\omega}_{T_1}$ is an appropriate Brillouin-zone-average rotary-mode frequency. Far below the phase transitions, $\bar{\omega}_{T_1}$ is expected to be temperature independent and a T^{-2} temperature dependence for T_1 is predicted. The data in Fig. 1 indicate that this condition obtains for temperature below 200 K. Above 200 K, the deviation of the T_1 data from the T^{-2} law reflects soft-mode behavior. The deduced temperature dependence of $\bar{\omega}_{T_1}$ is shown in Fig. 2. The actual numerical values of $\bar{\omega}_{T_1}$ should not be taken too seriously because it is extremely difficult to acquire an accurate value of the constant C. Rather, it is the substantial softening that is significant ($\bar{\omega}_{T_1}$ decreases by 66% as the temperature of CsPbCl$_3$ increases from 200 to 320 K). The reason that the zone-averaged rotary-mode frequency softens considerably more in CsPbCl$_3$ than in K$_2$PtBr$_6$ is believed to be related to the fact that in the former case, it is a zone-boundary phonon that softens, whereas in the latter case, a zone-center phonon is involved.

There are two further items of interest concerning the T_1 data obtained in $CsPbCl_3$. First, a thermal-hysteresis effect was observed in the vicinity of 320 K. The shape if the hysteresis loop depends on the thermal history of the sample. (The data shown in Fig. 1 were obtained as the sample temperature was increased. The spread in T_1 values observed at any temperature due to the hysteresis was sufficiently small so as to have no effect on the mode frequencies deduced in Fig. 2.) Hysteresis has also been noted in other experiments on $CsPbCl_3$. In particular, Busmundrud and Feder[15] noted such effects in their electrical-conductivity experiments. Second, for the data taken above 290 K, the return to equilibrium of the magnetization following an rf pulse occurs nonexponentially with time. The amount of the deviation from exponential behavior depends on the thermal history. The signal-to-noise ratio of the observed resonance was not sufficiently large to allow a reliable two time constant fit to be achieved. The observed behavior may be related to the formation of distorted phase dynamic clusters in the cubic phase and cubic phase clusters in the distorted phase.[16] In such a case, one relaxation time would be associated with the thermal fluctuations of the electric field gradient, and a second and shorter relaxation time with sudden variations of the electric field gradient as a particular small portion of the compound changes from a cubic to a distorted structure or vice versa.

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