Classification
 Physics Abstracts
 76.60E — 66.30H

^{19}F nuclear relaxation in an ionic conductor : TlSn_2F_5

W. Granier

Laboratoire de Chimie des Matériaux (*), E.N.S.C.M., 8, rue de l'Ecole-Normale, 34075 Montpellier, France

P. Bernier

Groupe de Dynamique des Phases Condensées (*), U.S.T.L., place Eugène-Bataillon, 34060 Montpellier, France

M. Dohri, J. Alizon and H. Robert

Laboratoire d'Electronique et de Résonance Magnétique (*), 24, avenue des Landais, 63170 Aubière, France

(Reçu le 22 décembre 1980, révisé le 3 mars 1981, accepté le 13 mai 1981)

Résumé. — Nous avons étudié la Résonance Magnétique Nucléaire du ^{19}F sur le composé TlSn_2F_5 , à différentes températures et fréquences. Alors que le T_1 mesuré présente pour $T < 358\text{ K}$ un comportement classique, tel qu'il est généralement observé sur les conducteurs ioniques, un saut soudain est observé pour $T \sim 358\text{ K}$ où intervient un changement de groupe d'espace du système. Pour des températures plus élevées, le comportement observé est caractéristique d'une très haute mobilité des fluors. Ces résultats sont comparés avec ceux obtenus par mesures de conductivité, qui montrent que ce composé est un des meilleurs conducteurs ioniques par ions F^- .

Abstract. — We have studied the ^{19}F NMR of the TlSn_2F_5 compound at various temperatures and frequencies. While the measured T_1 shows a classical behaviour for $T < 358\text{ K}$, as is generally observed in ionic conductors, it undergoes a sudden increase at $T \sim 358\text{ K}$ corresponding to a change in the crystallographic space group. For higher temperatures, the observed behaviour is consistent with a very high mobility of the fluorine atoms. These results are compared with those obtained by conductivity measurements which make this compound one of the best ionic conductors *via* the F^- ions.

Various papers, involving T_1 relaxation time measurements on the ^{19}F nuclei, have been performed recently particularly on compounds with the fluorite structure : CaF_2 [1], PbF_2 [2], BaF_2 [3] or on compounds with a derived structure such as PbSnF_4 [4]. Such studies have been undertaken in order to understand and to explain the origin of the fluorine mobility in these anionic materials.

Various criteria are likely to enhance the fluorine conductivity in ionic conductors :

- weak coordination of the fluorine ion,
- structures with vacancies,
- strong polarizability of the cations,
- low melting entropy.

We have chosen to add a cation polarizable fluoride to SnF_2 in order to increase its conductivity. Then we have investigated the various phases of the

system TlF-SnF_2 . It appeared that TlSn_2F_5 had a conductivity significantly higher than the other phases [5]. This fact probably correlates with the peculiar crystallographic structure of this compound [6].

In this paper we describe the NMR experiments performed on the ^{19}F nuclei of the TlSn_2F_5 compound. We have studied the temperature and frequency dependencies of the measured relaxation time T_1 , in order to get some information about the origin and characteristics of the ionic diffusion process. A comparison with conductivity measurements is given.

1. Experimental conditions. — TlSn_2F_5 has been prepared from $\text{SnF}_2 \alpha$ (OSI) and thallium carbonate (MERCK) in the presence of fluorhydric acid. During the cooling of the solution, crystals were obtained in the form of small plates. The dry products were kept in glass tubes under an argon atmosphere.

The NMR measurements have been performed

(*) Laboratoires associés au C.N.R.S.

using a Brüker S × P100 spectrometer (for the resonance frequencies $\nu = 16, 30$ and 80 MHz) and a home-made spectrometer of the Clark type [7] (for $\nu = 6.3$ MHz). The nuclear relaxation time T_1 of the ^{19}F atoms has been measured using the standard pulse sequences π , $\pi/2$ (free induction decay) or π , $\pi/2$, π (spin echo).

The temperature of the sample ($233\text{ K} < T < 423\text{ K}$) was controlled using a flow of heated dry air through a quartz cryostat. The regulation has been achieved with a classical PID technique. The accuracy on the determination of the sample temperature was of the order of $\pm 2\text{ K}$ while the stability of T was better than $\pm 0.5\text{ K}$.

Conductivity measurements have been performed up to 403 K by the complex impedance method between 5 Hz and 500 kHz . The samples were cylindrical pellets, compressed at 423 K . Gold electrodes were deposited by evaporation under vacuum.

2. Experimental results. — The nuclear magnetization recovery towards equilibrium has always been observed to be exponential, allowing us to define a unique T_1 . Figure 1 represents the dependence with the inverse temperature $10^3/T$ of the measured T_1

Fig. 1. — Variation with the inverse temperature $10^3/T$ of the measured T_1 on a Log scale, for various frequencies.

on a Log scale. In all cases the T_1 values are observed to decrease with the working frequency. It is also clear that there is an unusual behaviour which appears around $T = 358\text{ K}$ because over a small temperature range ($\sim 10\text{ K}$) the T_1 values strongly increase with

increasing temperature at least for the lowest frequencies. We then consider the two distinct temperature ranges $T < 358\text{ K}$ and $T > 358\text{ K}$.

1) $T < 358\text{ K}$.

Starting from the lowest temperature, the measured T_1 decreases with increasing T (low temperature regime), goes through a minimum value, which is well defined for $\nu = 6.3\text{ MHz}$, and then increases again (high temperature regime).

For the lowest frequency (6.3 MHz) the observed dependence of T_1 in the low and high temperature regimes are approximately symmetric with respect to the location of the minimum ($\sim 323\text{ K}$). For the other frequencies, the T_1 minimum as well as the high temperature region are less well defined because they are perturbed by the anomaly at 358 K .

Finally it is observed that in the low temperature region the frequency dependence of T_1 is roughly described by the law $T_1 \propto \omega^{3/2}$ (Fig. 2), where $\omega = 2\pi\nu$.

Fig. 2. — Frequency dependence of the measured T_1 at two distinct temperatures in the low temperature region (see text).

2) $T > 358\text{ K}$.

In this range T_1 increases with increasing temperature and is not very frequency dependent. We also note that the slopes of the temperature dependence of $\log T_1$ are not frequency dependent and their absolute values are significantly smaller than in the range $T < 358\text{ K}$.

3. **Discussion.** — The total observed behaviour, i.e. (i) the symmetry on both sides of the T_1 minimum for $\nu = 6.3$ MHz, (ii) the strong frequency dependence in the low temperature regime, and (iii) the weak frequency dependence in the high temperature region, suggests that an interpretation of our experimental results can be made using the Bloembergen, Purcell and Pound (BPP) theory [8].

We will discuss first the temperature range $T < 358$ K below the anomaly.

We suppose that there is an isotropic motion for the diffusing atoms and a diffusion process which can be characterized by a unique correlation time τ_c which obeys the law

$$\tau_c = \tau_0 \exp(E_a/K_B T)$$

where τ_0 is a constant and E_a the activation energy of the diffusion process.

In the low temperature region, which is characterized by $\omega\tau_c \gg 1$ in the BPP theory, the spin lattice relaxation time T_1 is given by

$$T_1 \propto \tau_0 \omega^2 \exp(E_a/K_B T).$$

The observation of a linear dependence between $\log T_1$ and T^{-1} (Fig. 1) allows us to define $E_a \sim 0.30 \pm 0.02$ eV.

Nevertheless the ω^2 dependence of T_1 which is expected in the case of the simple BPP theory is not observed. Figure 2 shows that the experimental dependence is close to $\omega^{3/2}$. As shown by Abragam [9], such a behaviour is expected for a diffusion system when $\omega\tau_c > 1$ (low temperature region) and when the details of the molecular dynamics, which control the magnetic relaxation, must be taken into account. This $\omega^{3/2}$ frequency dependence has been observed recently [10] for the proton relaxation on the compound $\text{TiS}_2(\text{NH}_3)$ where the NH_3 molecule experiences a two-dimensional diffusion between layers of titanium disulfide.

In the high temperature region, $\omega\tau_c \ll 1$, we have

$$T_1 \propto \tau_0^{-1} \exp - (E_a/K_B T).$$

Such a law is observed only when $\nu = 6.3$ MHz where the T_1 minimum and the high temperature branch can be defined (Fig. 1). In this case, the E_a value which can be deduced is very close to the one obtained in the low temperature region. The location of the T_1 minimum allows us to estimate $\tau_0 \sim 2.5 \times 10^{-13}$ s, which leads to the final expression

$$\tau_c \sim 2.5 \times 10^{-13} \exp \frac{0.3}{K_B T} (\text{s}).$$

For higher frequencies the T_1 minimum, as well as the high temperature branch are severely perturbed by the anomaly at 358 K (Fig. 1). The value obtained for the activation energy E_a must be compared to the

one obtained from a study of the temperature dependence of the electrical conductivity (Fig. 3). The value 0.52 ± 0.03 eV obtained for $T < 358$ K in this latter case indicates that the local motions of the F^- ions which can contribute to the nuclear relaxation are spatially restricted and do not contribute to the macroscopic conductivity. Such a behaviour is commonly observed for ionic crystalline conductors [4].

Fig. 3. — Variation of the Log of electrical conductivity versus $10^3/T$.

Let us now consider the temperature range $T > 358$ K, above the anomaly. In this case T_1 increases with increasing temperature (Fig. 1). The slope of the variation allows us to define an activation energy $E'_a \sim 0.19 \pm 0.02$ eV which is very close to the activation energy 0.22 ± 0.03 eV deduced from the temperature dependence of the conductivity (Fig. 3).

The sudden jump of the T_1 value observed around 358 K, at the lowest frequencies, has to be related to the strong increase in the conductivity which appears at the same temperature. In order to understand such a behaviour, calorimetric measurements have been performed on the material. Such measurements show a reversible thermal effect with a transition enthalpy of 520 ± 30 cal./mole. This transition is a first order process which corresponds to a structural change. TiSn_2F_5 , whose structure is rhombohedral with the space group $P3m1$ at room temperature (non centrosymmetric) shows a centrosymmetric structure with

the space group $P\bar{3}m1$ above 358 K. Such a change is confirmed by non linear optical measurements : we have observed that the transmission of laser light ($\lambda = 1.06 \mu$) through the sample was shifted to the green ($\lambda = 0.53$) part of the spectrum for $T < 358$ K.

In figure 4 we show the projection on the ab plane of the structure of KSn_2F_5 which is isostructural with $TlSn_2F_5$ and presents a better crystallinity [6].

Fig. 4. — Projection in the ab plane of the $TlSn_2F_5$ structure at room temperature.

The fluorine atoms F_1 and F_2 define short bonds to the Sn atoms (1.90 Å for Sn- F_1 and 2.04 Å for Sn- F_2 , respectively), F_5 and F_6 have medium bonds to the Sn atom (2.28 Å and 2.15 Å for Sn- F_5 and Sn- F_6 , respectively) and their occupancy is only one third. Finally, F_3 and F_4 present still longer bonds to the Sn atoms (2.43 Å and 2.46 Å for Sn- F_3 and Sn- F_4 , respectively) and their occupancy is only one half. This structure then shows a large number of vacancies. The fluor-vacancy distances are very short : 1.78 and 1.59 Å, while the normal observed fluor-fluor distance is about 2.60 Å. Such short distances explain the small τ_c value which is deduced from the T_1 measurements. As the diffusion is isotropic, the conductivity occurs in the plane (F_3 , F_5) and (F_4 , F_6).

We are then concerned with a conductivity within layers in the temperature range $T < 358$ K which becomes more efficient in the temperature range $T > 358$ K not only because the symmetry is enhanced, leading to a smaller activation energy, but also because the fluorine atoms F_1 and F_2 can participate to the process. The transition at 358 K can then correspond to a « melting » of the anionic sub-lattice, leading to the high conductivity value of $5 \times 10^{-2} (\Omega \cdot \text{cm})^{-1}$ at 393 K, which makes $TlSn_2F_5$ the best known ionic conductor through F^- atoms at this temperature.

These results must be compared to those obtained on $PbSnF_4$ which has a derived fluorite structure [11]. In this case, at low temperatures ($T < 270$ K), the dominant diffusion contribution is the hopping motion between normal sites in the lattice, which is favoured by the presence of a great number of vacancies. We are then concerned with a diffusion mechanism along fluorinated chains as generally observed on systems with the fluorite structure. At intermediate temperatures ($270 < T < 330$ K) an exchange between the fluorine atoms in normal and interstitial positions appears. At high temperature ($T > 330$ K) this exchange becomes more and more efficient leading to a quasi « melting » of the anionic sub-lattice.

4. Conclusion. — In this study we have shown that ^{19}F relaxation time and conductivity measurements on $TlSn_2F_5$ give with a good agreement information about the diffusion process of the F^- ions. We have determined the activation energies and shown that, for $T > 358$ K, probably all the F^- ions participate in the diffusion process, as the activation energies deduced from relaxation and conductivity measurements are roughly equal. At low temperatures the results are compared with the crystallographic data and suggest a diffusion of the F^- ions within layers, rather than diffusion along fluorinated chains as observed on systems with the fluorite structure. Measurements performed on single crystals in order to confirm these points are in progress.

References

- [1] BOOTH, R. J., MUSTAFA, M. R. and MCGARVEY, B. R., *Phys. Rev. B*, **17**, n° 11 (1978) 4150.
- [2] BOYCE, J. B., MIKKELSEN, J. C. and O'KEEFFE, M., *Solid State Commun.* **21** (1977) 955.
- [3] FIGUEROA, D. R. and STRANGE, J. H., *J. Phys. C. Solid State Phys.* **9** (1976) 203.
- [4] VILLENEUVE, C., ECHEGUT, P., LUCAT, C., REAU, J. M. and HAGENMULLER, P., *Phys. Status Solidi (b)* **97** (1980) 295.
- [5] PEREZ, G., Thèse, Montpellier (Juillet 1980).
- [6] VILMINOT, S., PEREZ, G., GRANIER, W. and COT, L., *Rev. Chim. Minér.*, to be published.
- [7] CLARK, W. G., *Rev. Sci. Instrum.* **35** (1964) 316.
- [8] BLOEMBERGEN, N., PURCELL, E. M. and POUND, R. V., *Phys. Rev.* **73** (1948) 679.
- [9] ABRAGAM, A., *Principles of nuclear magnetism*, (Oxford University Press) 1961, p. 461.
- [10] KLEINBERG, R. L. and SILBERMAGEL, B. G., *Solid State Commun.* **33** (1980) 867.
- [11] VILMINOT, S., GRANIER, W., COT, L., *Solid. State Ionics*, to be published.