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^{19}F NUCLEAR RELAXATION STUDY OF THE FLUORITE SYSTEM: $K_{0.36}Bi_{0.64}F_{2.28}$[*].

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Measurements of the ^{19}F nuclear relaxation times T_1 and T_2 are reported for the fluorite-structured: $K_{0.36}Bi_{0.64}F_{2.28}$ single crystal, as a function of temperature and frequency. The main features of our experimental results are as follows: a) the presence of a broad minimum and a highly assymetric shape in the T_1 vs T^{-1} curve; b) a strong dependence of T_1 with the nuclear Larmor frequency at low temperatures; and c) the presence of a minimum of T_2 in the high temperature region. The NMR relaxation data is found to reflect the presence of a distribution of barrier energies for ionic motion characteristic of an inhomogeneous diffusion process.

1. INTRODUCTION

The study of crystals with the fluorite structure that exhibit anion conductivities well bellow their melting temperatures has attracted considerable attention[1-6]. Particularly, the ternary compounds with the fluorite structure ($R_xM_{1-x}F_{2x+1}$), have a much higher ionic conductivity at room temperature than the binary compounds due to their built-in defect structure[4]. Fluoride ion conductivities of the $K_xBi_{1-x}F_{2x+1}$ system have been recently measured, yielding an Arrhenius-like behavior over all temperature range with an activation energy of 0.3 to 0.4 eV[2,3,4]. A question of central importance for understanding the microscopic mechanism of these K-Bi fluoride systems is the effect of the crystal disorder upon the ionic motion. The crystals are strongly disordered on a microscopic scale because of local charge compensation since the cation sites in the fluorite structure are randomly occupied by the ions K^+ and Bi^{3+}.

Such information may be achieved by a Nuclear Magnetic Resonance (NMR) study of the nuclei of the diffusing ion. This technique proved to be an excellent method in extracting the microscopic character of the ion motion in superionic conductors[5,6,7].

This paper reports on the NMR study of the superionic conductor: $K_{0.36}Bi_{0.64}F_{2.28}$, as a function of the Larmor frequency and temperature, (in the same range of the conductivities studies). The mobile ion nuclear, ^{19}F, with I = 1/2 has a large gyromagnetic ratio and is 100% abundant. The ion nuclei ^{39}K, ^{41}K and ^{209}Bi have a much smaller one. Our results show a clearly assymetric shape in the $\ln T_1$ vs T^{-1} curve and we suggest that it is a characteristic of strongly disordered systems. Such a disordered structure might confront the moving ion with different barrier heights leading to an inhomogeneous diffusion process. A tentative description of this situation in terms of a distribution function for the activation energies is given.

2. EXPERIMENTAL

$K_{0.36}Bi_{0.64}F_{2.28}$ single crystals were grown from the melt by the horizontal zone technique and Bridgman method[4]. The sample used for NMR measurements was cut from zone grown material. ^{19}F T_1 and T_2 measurements were made using a conventional pulsed NMR spectrometer. A high Q, variable temperature resonator tunable in a wide frequency band was built. Kanthal wire and Saureisen # 78 high temperature cement were used for the heater. The coil-heater assembly was thermally isolated and housed in a water cooled box. A thermocouple sensor and a current regulator circuit were used to control the temperature. A signal averager PAR model 4202 was used to improve the signal-to-noise ratio.

T_1 was measured using standard techniques at Larmor frequencies of 10.5, 23.6 and 35.8 MHz. For T_2, spin echo technique was used at 23.6 MHz. These relaxation times are shown in Fig. 1 as a function of reciprocal temperature, from room temperature to 450 °C. The result can be summarized as follows:

a) The $\ln T_1$ vs $1/T$ curve exhibits a broad minimum at $T \simeq 200$ °C.
b) The $\ln T_1$ curve also shows an assymetric shape very similar to that encountered in Na-β-Alumina[10]. The measured T_1 passes from a low T frequency - dependent region to a frequency - independent one, where T_1 increases with increasing T.

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c) The $\ln T_2$ vs $1/T$ curve exhibits a behavior qualitatively similar to that reported for PbF_2 (pure and doped)[7,9]. Motional narrowing is already apparent at 50 °C. The high T region, above 200 °C, shows a minimun in T_2 at 350 °C.

3. DISCUSSION

Since ^{19}F has nuclear spin 1/2, it couples to the lattice only via its magnetic moment. For a pure material, this coupling is dominated by the nuclear dipole-dipole interaction, modulated by the motion of the fluoringe nuclei. The ^{19}F relaxation rates are given by the Bloembergen-Purcell-Pound (BPP)[11] model theory, and with the assumption of an exponential correlation function, and a single correlation time with an Arrhenius behavior, one expects to find a symmetrical V-shaped T_1 curve; i.e. T_1 should displays minima as a function of 1/T with numerically identical slopes on either side, that are given by the activation energy for the ionic motion.

The above assumptions obviously do not apply to our systems, since the data in Fig. 1 show a clearly assymetric minimun in T_1. This is also true for the reported behavior of ^{23}Na relaxation in Na-β-Alumina[10] and one is thus lead to assume that it is a characteristic of strongly disordered systems. Disorder in the present case comes about due to the random occupation of cationic site of the fluorite structure by either K^+ or Bi^{3+} ions. Such a disordered structure might confront the moving ion with different barrier heights leading to an inhomogeneous diffusion process. In the abscence of paramagnetic scattering centers[9] the basic BPP ideas are still valid and attempts could be made to describe the T_1 behavior introducing a detailed description of these complicated percolation paths involving different activation energies.

A simple phenomenological approach was introduced for Na-β-Alumina by Walstedt et al[10], which essentially consists of introducing a continuous distribution of activation energies. Here we follow these authors since we believe that this approach leads to a usefull parametrization of the problem.

According to Ref. 10 we write for T_1

$$T_1^{-1} = C \int dU \, \frac{G(U)\tau}{1 + \omega_o^2 \tau^2} \qquad (1)$$

where G(U) is a distribution function, τ is the correlation time given by $1/\tau = \nu(U)e^{-U/kT}$ and $\nu(U) = \nu_0(U/U_0)^{1/2}$ for sinusoidal barrier shapes. U_0 is the peak activation energy and ω_0 is the Larmor frequency. The solid lines in Fig.1 are fit of Eq.(1) to the data using a Gaussian distribution function for G(U). The parameters from the fitted curve are $U_0 = 0.31$ eV, $\Delta U_{1/2} = 0.058$ eV, $\nu_0 = 1.25 \times 10^{12}$ (sec^{-1}) and $C = 3 \times 10^{10}$ (sec^{-2}).

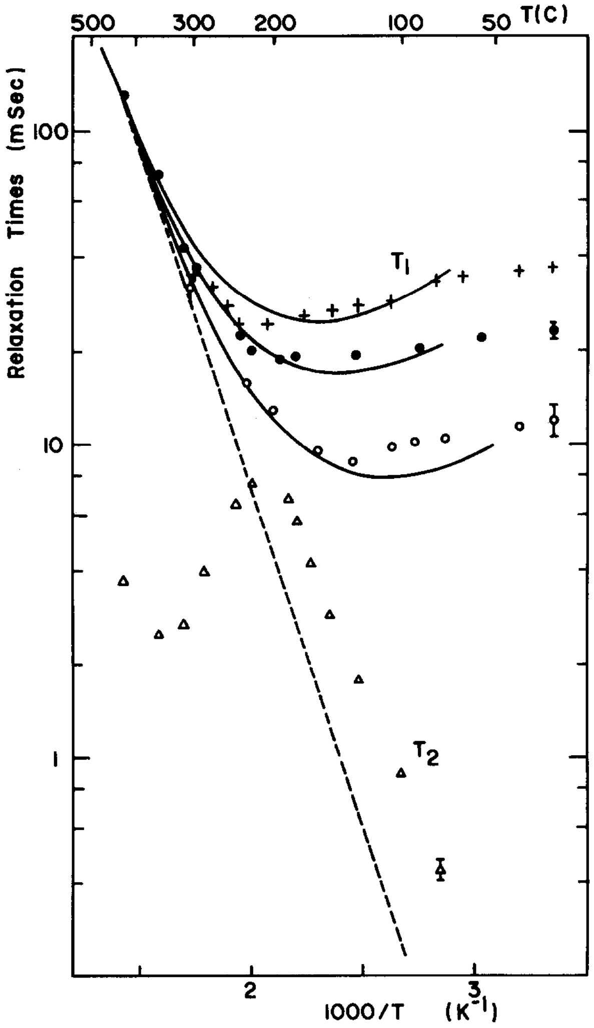

Figure 1:

NMR relaxation times of ^{19}F as a function of reciprocal temperature in $K_{0.36}Bi_{0.64}F_{2.28}$. T_1: +35,8 MHz Larmor frequency. ● 23.6 MHz, o 10.5 MHz. T_2: Δ23.6 MHz. The solid line is a fit of Eq.(1) to the data, using a Gaussian distribution function for G(U). The dashed line is the limit $\omega_0 = 0$ in Eq.(1).

The observed dependence of T_1 with Larmor frequency and temperature are well predicted by the phenomenological approach presented above. We note that the peak value $U_0 = 0.31$ eV is lower than the activation energy obtained from conductivity data, $U_0 = 0.37$ eV. This would mean that a good deal of ion motion affecting the relaxation times does not contribute to the conductivity. This same conclusion also reached for β-Alumina is understandable since confined ionic motion plays a role in NMR while does not contribute to the bulk conduction process.

It is interesting to note that a BPP model with a single activation energy applied to the T_2 data on the low temperature side gives $U_0 = 0.35$ eV closer to the bulk value.

On the other hand setting $\omega_0 = 0$ in Eq.(1) one can find the temperature dependence of T_2. This is plotted in Fig.(1) (dashed line). This approximately describes the low temperature behavior of T_2 although the absolute values are not reproduced.

The value $\nu_0 = 1.25 \times 10^{12}$ sec^{-1} obtained for the attempt frequency from T_1 data is consistent with the observation of a Raman active mode at 45 cm^{-1}.(12)

As to the high temperature results we notice that the T_1 data show a frequency independent behavior that could be accounted for by a BPP model using a single correlation time with an Arrhenius type temperature dependence. The corresponding activation energy equals the value 0.31 eV used to fit T_1 to Eq.(1). This value is lower than the one found above from T_2. This result might be related to a reported change in the slope in the thermal dependence of the conductivity, at T $\simeq$ 300 °C, as well as a transition observed by Differential Thermal Analysis measurements, at the same temperature[4].

Starting at T $\simeq$ 200 °C, T_2 decreases with increasing T, reaching a minimun value at T $\simeq$ 350 °C. This behavior may be attributed to the magnetic impurity - generated "encounter" mechanism proposed by Vernon et al[8,9]. To test this possibility a sistematic study with controlled impurity levels would be required. It should be mentioned also that the measurements reported by Shafer and Chandrashektar[3] in the $KBiF_4$-BiF_3 system, show a composition independent conductivity at about 360 °C. These authors mention that this occurrence may originate from the formation of a critical concentration of clusters of interstitial fluoride ions and substituted cations at this temperature region. A similar phenomena was also observed in $K_{0.39}B_{0.61}F_{2.2}$ dopped with either Pb, Th, or O at about the same temperature[4].

Although the effect of this kind of clusters upon the Fluorine nuclear relaxation has not yet been examined, it is possible that their presence might offer an alternative explanation for the observed T_2 behavior at this temperatures.

4. CONCLUSIONS

The present results suggest that a behavior characteristic of disorderer systems may be expected for T_1 in the low temperature side of the minimun. A much better understanding of this question is necessary to allow a consistent description of both T_1 and T_2 in this temperature region. Finally, the high temperature region should be further studied both theoretically and experimentally to investigate possible relaxation mechanism which can compete with magnetic impurities in this temperature region.

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