Nuclear Relaxation and Slow Diffusive Motions in CaF_2 and NaF

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Fluorine relaxation times T_{1Z}, T_{1D} and T_2 are measured as functions of temperature in single crystals of CaF_2 and NaF. Typical quantities like the activation energy for vacancy diffusion and the formation energy of defect pairs are deduced and reported.

Introduction

Magnetic resonance is a well known tool for the investigation of atomic and molecular motions in solids and a large amount of work has been done in the past on this subject by studies of Zeeman (T_{1Z}) spin-lattice relaxation time and dipolar line widths (T_2). More recently, the power of the NMR method has been still considerably improved by the measurements on rotating frame[1, 2] $T_{1\varrho}$ and dipolar (T_{1D}) relaxation rates which are particularly sensitive to extremely slow spin motions in solids.

This last method, together with conventional T_{1Z} and T_2 measurements is applied in this paper for the detection of slow vacancy diffusion in monocrystals of CaF_2 and NaF.

Detailed information about typical quantities like the activation enthalpy for vacancy diffusion and the formation energy of defect pairs is obtained.

Experimental

All the experiments were made on the fluorine atoms with a pulse spectrometer tuned at 15 Mc. T_{1Z} was measured by the conventional 90°-t-90° pulse technique.

For T_{1D}, a $90°\text{-}T\text{-}45°_{90°}\text{-}t\text{-}45°$ pulse sequence was used as proposed by Jeener[3].

The quantity reported here as T_2 is simply the time required by the free precession following a 90°-pulse to decay to half its maximum value.

The investigated temperature region extends from 300 °K to 1300 °K approximately and one of the major difficulties encountered in the T_{1D} measurement is due to the poor signal to noise ratio. To overcome this a fast transient recorder (Biomation 610) was used in connection with an I.B.M system 7 computer in an accumulation program. Ten to twenty passages were necessary for an accurate determination of each point of the amplitude-time relaxation curve. Temperatures were measured with two Pt, Pt-Rh thermocouples placed on both sides of the crystal. The mean value of the two readings was taken and differences of a few degrees were typical. Finally, the temperature was maintained constant to better than 0.5 °K with an automatic proportional regulating loop.

Measurements and Discussion

A) CaF_2

The Zeeman and dipolar relaxation times of the F nuclei were measured from 290 °K up to 1,220 °K. The crystal investigated is a Harshaw "pure" monocristal oriented with the (100) axis parallel to the external magnetic field. The basis we take for the interpretation of our results is the well known fact[4] that the main defect in CaF_2 is the anti-Frenkel disorder, involving equal concentrations of negative ion vacancies and interstitials. The Zeeman relaxation curve (Fig. 1) is divided in three temperature regions. From 290 °K to 530 °K, relaxation is governed by the presence of paramagnetic impurities and by the process of spin diffusion. The extremely slow temperature variation of T_{1Z} and the fact that the ratio T_{1Z}/T_{1D} is equal to three in this region confirm this interpretation.

Between 530 °K and 846 °K, a straight line semilog plot of $1/T_{1Z}$ can be obtained if the actual measured rates are corrected for the contribution due to paramagnetic impurities. The activation energy in this region is found to be 0.65 eV. Like other authors[5] we think that the behaviour of T_{1Z} is here controlled by the diffusion of extrinsic vacancies, and the measured activation energy is directly related to the anion vacancy random jump process.

Above 840 °K, the Zeeman relaxation rate goes through a maximum with slopes corresponding to an "effective" activation energy of 2.0 ± 0.3 eV.

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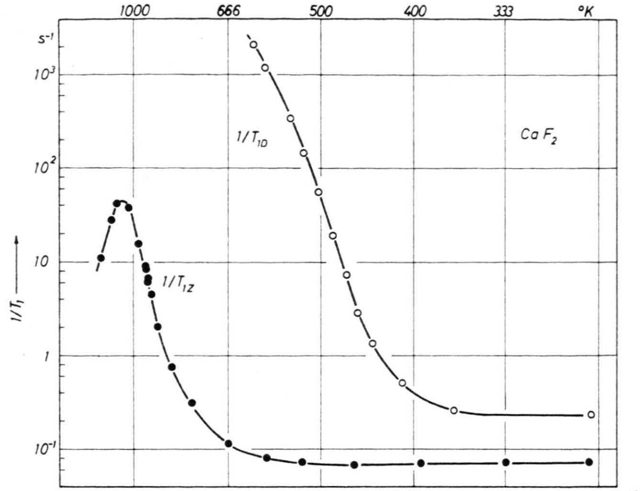

Fig. 1. Measured values of T_{1Z} and T_{1D} versus $10^3/T$ in CaF$_2$ oriented with a (001) axis parallel to the field.

This region is governed by the diffusion of thermally produced vacancies and the measured slope is given by $E_F/2 + E_V^-$, where E_F is the formation enthalpy of a vacancy-interstitial pair and E_V^- the diffusion activation energy of a fluorine anion vacancy. From this interpretation we obtain $E_F = 2.7$ eV in good agreement with Ure's result[4] of 2.82 eV. The maximum Zeeman relaxation rate is expected to appear when the correlation time, τ, is of the order of the Larmor Period (10^{-8} sec in our case). If there are N_V jumping vacancies the correlation time is approximately given by:

$$\tau = \tau_V (N/N_V)$$

where τ_V is the meantime a vacancy "sits" between two jumps and N the total number of sites. Ure has reported values for the entropy of formation of an anti Frenkel defect. The ratio N_V/N can thus be evaluated from the relation:

$$N_V = \exp\{-G_F/2\,k\,T\} \cdot (N\,N')^{1/2} \qquad (1)$$

where N' is the number of interstitial sites and G_F is the Gibbs free energy change accompanying the formation of the defect. In this way we find $\tau_V(10^3/T = 0.93)\ 5 \cdot 10^{-12}$ sec.

We now turn to the discussion of the dipolar relaxation rate. From 290 °K to 370 °K paramagnetic impurities govern the phenomena. Above 420 °K the rate increases steadily but cannot be characterised by a unique activation law in the whole range. At 625 °K, T_{1D} is as short as 500 μs indicating the vicinity of the maximum. Higher temperature points could not be taken because of prohibitively small signal to noise ratio. At 450 °K the relative number of thermal vacancies can be estimated from (1) to be as low as 10^{-13} and the T_{1D} behaviour is most probably governed by the larger amount of defects characteristic of the extrinsic region. The variation of the activation energy for vacancy diffusion in this region has already been noted in the electrical conductivity (σ) measurements of Ure who discusses also the possible origin of this effect (thermal expansion of the crystal, trapping of vacancies by impurities ...).

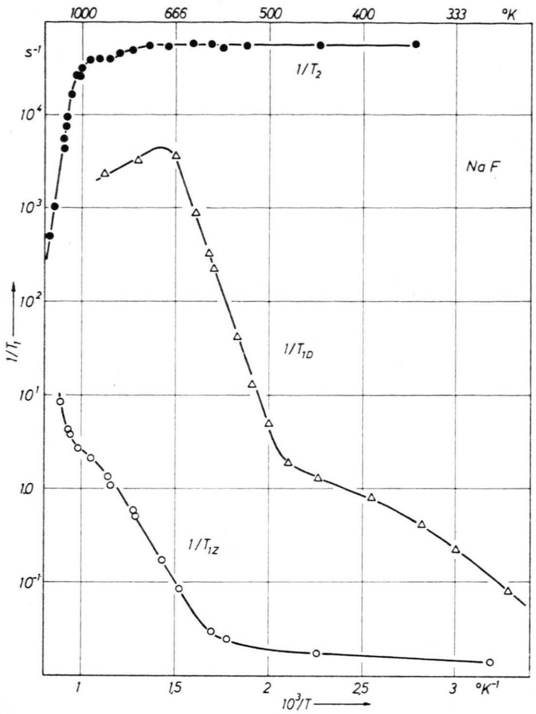

Fig. 2. Measured values of T_{1Z}, T_{1D} and T_2 versus $10^3/T$ in NaF oriented with a (001) axis parallel to the field.

Table 1. Activation energy for fluorine vacancy jumps and energy of formation of anti-Frenkel pairs in pure CaF$_2$. I: R. J. Lisiak and P. P. Mahendroo[5]; T_{1Z} measurements. II: R. W. Ure[4]; conductivity measurements. III: This work.

	I		II		III	
T °K	E_F	E_V^-	E_F	E_V^-	E_F	E_V^-
600 – 900		0.36		0.52		0.65
873				0.52		0.65
673				0.63		0.65
573				0.74		0.86
473				0.87		1.2
900 – 1200			2.82		2.7	

In Table I, we collected our experimental results and compare them with σ and T_{1Z} measurements by other authors.

The general agreement with conductivity is thus quite good. The slow motion technique extends the informations about the extrinsic region down to 450 °K. At this temperature, T_{1D} is correctly described by the Slichter and Ailion[1] relation:

$$1/T_{1D} = (2/\tau)\,(1-p) \tag{2}$$

where $(1-p)$ is a factor of order one. The angular dependance of this factor has been calculated[6] for various diffusion processes. For vacancy diffusion in a cubic sublattice it turns out that $(1-p)$ is practically independent of the angle: $a = (1-p)_{0°}/(1-p)_{45°} = 1.05$. Experimentally the ratio a was measured as 1.09 in our crystal, confirming thus our interpretation.

B) NaF

The main thermal defects in sodium fluoride are of the Schottky type, consisting of equal numbers of positive and negative ion vacancies. Our results about T_{1Z}, T_{1D} and T_2 for a "pure" crystal with a (100) direction parallel to the field are shown in Figure 2. The interpretation of these experiments was greatly simplified by the recent work of Bauer and Whitmore[7] concerning the ionic conductivity in this crystal. These authors have reported values for the formation enthalpy and entropy of a Schottky pair allowing an estimation of the number of thermal defects and the assignment of our experiments to the extrinsic or intrinsic region. Below 580 °K, the paramagnetic impurities govern the T_{1Z} behaviour. Between 580 °K and 950 °K, the Zeeman relaxation shows an activation energy of 0.8 eV attributed to the diffusion of cation vacancies produced by impurities in the crystal. The shallow "maximum" at 960 °K may correspond to the maximum rate associated with that motion. Above 960 °K, the relaxation rate sharpens due to the onset of anion vacancy diffusion which is strongly confirmed by the sudden and abrupt narrowing of the absorption line indicated by our T_2 measurements.

Below 480 °K, the dipolar relaxation rate is thought to be due essentially to the presence of paramagnetic impurities and no special effort was made to understand better the experimental behaviour in that region. Above 480 °K, T_{1D} is characterised by an activation energy of 1.05 eV. The relative number of thermal defects calculated from the data of Ref.[7] gives $N_V/N \sim 10^{-11}$ ($T = 480$ °K) and we assign thus the T_{1D} behaviour to the diffusion of cation vacancies in the extrinsic region. The fact that the responsible motion in this region is cation vacancy diffusion is also confirmed by the small line narrowing observed at 750 °K almost in concordance with the dipolar maximum rate temperature (700 °K).

Finally, above 1000 °K, T_2 is characterised by an activation energy of 2.65 eV. This is a clear indication for the onset of diffusion of thermal anion vacancies. The enthalpy for formation of a Schottky defect is reported in Ref.[7] as 2.56 eV, which combined with our result indicates an activation energy for anion diffusion of 1.37 eV.

In Table 2 we collected our results and compare them with those of Ref.[7] obtained by thermal conductivity.

Table 2. Values of the formation energy E_F of a Schottky pair, and of the activation energies for cation E_{V^+} and anion E_{V^-} vacancy diffusion in NaCl. I: C. F. Bauer and D. H. Whitmore. II: This work.

I				II		
E_F	E_F	E_{V^+}	E_{V^-}	E_F	E_{V^+}	E_{V^-}
2.95	2.56	0.97	1.54		1.05 (T_{1D}) 0.8 (T_{1Z})	1.37

We think that our value for E_{V^+} as determined from T_{1Z} could be a little to low due to the vicinity of the maximum and the agreement with conductivity measurement is then quite good. On the other hand, a rather large discrepancy exists between our value of E_{V^+} and the value reported by Persyn and Nolle[8] (0.52 eV) on the basis of T_{1Z} measurements.

Finally the shape of the free decay following the 90° pulse used for the T_2 determination was recorded. Beats are present up to 1000 °K, the temperature at which a sudden change of the decay to the exponential form is noticed. The disappearance of these coherence effects, is of course due to the rapid diffusion of the F^- vacancies.

Conclusion

The determination of various parameters associated with the diffusion of point defects in CaF_2 and NaF has been achieved from fluorine relaxation time measurements. Because of the high sensitivity of the dipolar relaxation to slow motions, more precise information about these parameters could be obtained in the low temperature (extrinsic) region.

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