

Proton and Fluorine Spin-Lattice Relaxation in Polycrystalline CoSiF₆ · 6H₂O

H. Rager

Institut für Mineralogie, Petrologie und Kristallographie, Philipps-Universität Marburg

Z. Naturforsch. **39a**, 111–112 (1984); received October 19, 1983

The spin-lattice relaxation times $T_1(^1\text{H})$ and $T_1(^{19}\text{F})$ in CoSiF₆ · 6H₂O have been measured at 30 MHz in the temperature range 150 K ≤ T ≤ 400 K. Both $T_1(^1\text{H})$ and $T_1(^{19}\text{F})$ decrease sharply at the phase transition temperature of 246 K (cooling cycle). The main relaxation mechanism is assumed to be an Orbach process. From the T_1 data an average splitting of the Co²⁺ ground state of about 400 cm⁻¹ in both phases is obtained. The splitting is mainly caused by spin orbital coupling.

The well known phase transition in CoSiF₆ · 6H₂O which occurs at 246 K in the cooling cycle does not affect the nuclear magnetic resonance line width very much [1]. An investigation of the ¹⁹F nuclear spin-lattice relaxation times, $T_1(^{19}\text{F})$, gave no clear evidence for this either [2]. The purpose of this note is, therefore, to report the relaxation times $T_1(^1\text{H})$ and $T_1(^{19}\text{F})$ in CoSiF₆ · 6H₂O, which clearly show the phase transition. Moreover, from the T_1 data information on the Co²⁺ ground state splitting in both phases due to ligand field and/or spin orbital coupling is expected.

The relaxation times were measured at 30 MHz using the 90°, τ, 90° pulse method. The temperature was varied between 150 K ≤ T ≤ 400 K with an accuracy of ± 1 K. The temperature dependence of $T_1(^1\text{H})$ and $T_1(^{19}\text{F})$ is satisfac-

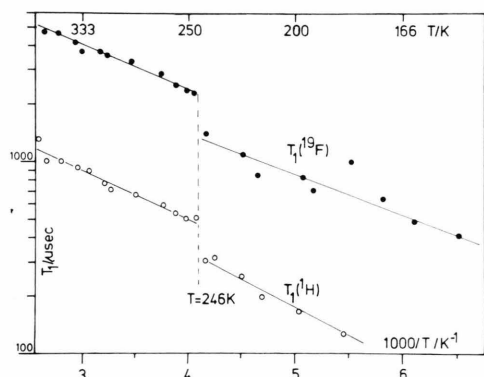


Fig. 1. Spin-lattice relaxation times $T_1(^1\text{H})$ and $T_1(^{19}\text{F})$ in CoSiF₆ · 6H₂O as a function of the reciprocal temperature. The solid lines were calculated using the relation $T_1(I) = a(I) \exp(-\Delta(I)/T)$, $I = ^1\text{H}, ^{19}\text{F}$, and the parameters listed in Table 1.

Reprint requests to Dr. H. Rager, Institut für Mineralogie, Petrologie und Kristallographie, Philipps-Universität Marburg, Lahnberge, D-3550 Marburg.

torily described in both phases by a relation of the type $T_1 = a \exp(-\Delta/T)$. Thus, the relaxation is assumed to occur through an Orbach process which was already supposed by Birkeland and Svare [2]. In the above relation the factor a is different for the proton and fluorine spin system whereas Δ is given by the splitting of the Co²⁺ ground state and, hence, independent of the spin system. Nevertheless, in practice $T_1(^1\text{H})$ and $T_1(^{19}\text{F})$ were fitted to the relation using $\Delta(^1\text{H})$ and $\Delta(^{19}\text{F})$ as fit parameters. This procedure yielded $\Delta(^1\text{H})$ larger than $\Delta(^{19}\text{F})$ (Table 1). Taking into account the limit of error, an average Δ value of 400 cm⁻¹ seems to be reasonable. The essential result of this procedure is, however, that both $\Delta(^1\text{H})$ and $\Delta(^{19}\text{F})$ are virtually constant over the whole temperature range investigated. This indicates that the splitting of the Co²⁺ ground state involved in the relaxation process is not affected very much by the phase transition. In contrast, the colour of CoSiF₆ · 6H₂O varies from pink to yellow at 246 K (cooling cycle) which gives evidence for a different splitting of the Co²⁺ states in both phases.

To understand this, the structure of CoSiF₆ · 6H₂O has to be considered. As pointed out by Ray et al. [3], the deviation of the hexaquo complex from a regular octahedron is very small in the high temperature form. The low temperature form of this complex may also be regarded as almost regular. A strict O_h symmetry for the Co(H₂O)₆²⁺ cation was even assumed by Ferguson [4], essentially because he observed no polarization in the crystal spectrum at 77 K. Thus, the irregularity in the hexaquo complex seems to be negligible in both phases and, hence, its local symmetry may be regarded as approximately cubic. The splitting of the Co²⁺ ground state then results mainly from spin orbital coupling and not from ligand field effects. This is in agreement with the discussion of the magnetic properties of CoSiF₆ · 6H₂O given by Gerloch and Qusteded [5]. These authors pointed out that a small angular distortion of the water octahedron will lead to a dominance by spin orbital coupling in the ⁴T_{1g}(F) ground state splitting. At the same time, however, even a small distortion may cause a significant splitting of the excited ⁴T_{2g}(P) state. According to this the change in colour at 246 K results from the different splitting of the excited Co²⁺ states in both phases whereas the ground state splitting remains constant.

In a strict cubic symmetry the spin orbital interaction splits the Co²⁺ ground state into three sublevels where the splitting between the two lowest levels is $\delta = 9/4 |\lambda|$. Taking the free ion value of $\lambda = -180 \text{ cm}^{-1}$ we obtain

Table 1. Parameters calculated from the temperature dependence of $T_1(^1\text{H})$ and $T_1(^{19}\text{F})$ in CoSiF₆ · 6H₂O using the relation $T_1(I) = a(I) \exp(-\Delta(I)/T)$, $I = ^1\text{H}, ^{19}\text{F}$, and a least-squares computer program. The maximum error is ± 20%.

	¹ H		¹⁹ F	
	$a \cdot 10^3$ sec	Δ cm ⁻¹	$a \cdot 10^3$ sec	Δ cm ⁻¹
$T > 246 \text{ K}$	6.7	460	18.8	360
$T < 246 \text{ K}$	4.4	450	11.6	360

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$\delta = 405 \text{ cm}^{-1}$. The agreement of δ with the average A value is surprising. It could be meaningless if one takes the above approximations into account. However, for the low temperature form of $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ Abragam and Pryce [6] calculated $\delta = 390 \text{ cm}^{-1}$ also assuming a nearly cubic field. Pryce [7] found $\delta = 305 \text{ cm}^{-1}$ for Co^{2+} in cubic MgO . Thus, the splitting of the Co^{2+} ground state in $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ obtained from relaxation time measurements is of the proper magnitude.

The free ion value of λ was taken for the above discussion, although usually λ is reduced by the covalent portion of the metal ligand bond [8]. Therefore, two experimental results should be emphasized which support at least a high λ value. The first is the large hyperfine splitting parameter $A = 95 \text{ G}$ obtained from electron paramagnetic resonance

measurements on Mn^{2+} in $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ [9]. As pointed out by several authors [10, 11], a large A value corresponds to a high ionicity of the metal ligand bond. The second is the unobserved shift of the ^1H and ^{19}F nuclear magnetic resonance in this compound, i.e. the delocalization of the unpaired Co^{2+} electron spins is small. Thus, both results indicate Co^{2+} as being mainly ionic, which in turn should lead to a high λ value.

Finally, it should be noted that in the similar compound $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ a phase transition occurs at about the same temperature. However, in $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ T_1 increases [12] whereas in $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ T_1 decreases sharply at the phase transition. The question why the effects of the phase transition on T_1 are opposite in the two similar compounds cannot be answered at the moment.

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