# Influence of Hydrostatic Pressure on the Zero-Field Splitting in NiSnCl$_6$·6H$_2$O

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The dependence of the crystal-field splitting parameter $D$ in NiSnCl$_6$·6H$_2$O on hydrostatic pressure was determined by the electron paramagnetic resonance method, for the pressures up to 500 MPa. The derivative $(\partial D/\partial p)_T$ as well as the temperatures and pressures at which the $D$-parameter reaches zero, were determined. The molecular mechanism responsible for the temperature and pressure changes of the $D$-parameter is similar to that one observed in the isomorphic NiSiF$_6$·6H$_2$O.

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## 1. Introduction

Nickel chlorostannate hexahydrate, NiSnCl$_6$·6H$_2$O, belongs to the trigonal space group $R\bar{3}$ [1] with one molecule in the rhombohedral unit cell. The [Ni(H$_2$O)$_6$]$^{2+}$ and [SiF$_6$]$^{2-}$ complex ions are arranged in CsCl-like structure. Each water octahedron has a small trigonal distortion. The trigonal crystalline field component splits the spin triplet of Ni$^{2+}$ ($S = 1$) ion into a singlet and a doublet. This splitting, represented by a zero-field splitting parameter $D$, was measured by the electron paramagnetic resonance method [2–4] as a function of temperature between 4.2 and 370 K [4]. The value of $D$ decreases rapidly with increasing temperature, reaching zero at 338 K and becoming negative at higher temperatures. In the vicinity of room temperature the variation is linear with the coefficient $(\partial D/\partial T)_p = -0.0020(1)$ cm$^{-1}$ K$^{-1}$.

In contrast to NiSnCl$_6$·6H$_2$O, in the isomorphic crystal NiSiF$_6$·6H$_2$O the $D$-parameter is negative under atmospheric pressure and its magnitude increases

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with increasing temperature [5]. For this compound, hydrostatic pressure EPR measurements at room temperature show that under pressure the value of $D$ is considerably reduced, reaches zero and changes its sign at 620 MPa [6]. On the basis of these results, the geometrical contribution (volume and unit cell shape) to the crystalline field splitting was separated from the dominant phonon contribution. Our recent EPR pressure study of $NiSiF_6 \cdot 6H_2O$ performed over the temperature range $90-190$ K has shown that there is an interval of temperatures and pressures in which $D$ becomes zero and the line width considerably decreases [7].

This unusual pressure behaviour of the $D$-parameter in $NiSiF_6 \cdot 6H_2O$ was the main reason to take up a similar study for nickel chlorostannate. So far no pressure studies have been performed for this compound. The aim of this study is to determine the dependence of the $D$-parameter on pressure. We put special emphasis on the range of temperatures and pressures, in which the $D$-parameter is small, passes through zero and changes the sign. The pressure and temperature behaviour of the $D$-parameter in $NiSnCl_6 \cdot 6H_2O$ is compared to that in nickel fluosilicate and is discussed in terms of phonon and geometrical contributions.

## 2. Experiment and results

EPR measurements at the frequency 9.4 GHz under hydrostatic pressure were carried out on both single crystal and crystalline powder sample of $NiSnCl_6 \cdot 6H_2O$ using a special appliance connected to a standard spectrometer [8, 9]. Single crystals of the compound were grown from an equimolar aqueous solution of $NiCl_2$ and $SnCl_4$ by slow evaporation at 30°C. The single crystal was placed into the sample hole of the corundum-filled resonator with the trigonal symmetry axis along the direction of the external magnetic field $\boldsymbol{B}$.

The EPR spectrum is described by an axially symmetric spin-Hamiltonian of the form

$$H = g_\parallel \beta B_z S_z + g_\perp \beta (B_x S_x + B_y S_y) + D\left(S_z^2 - \tfrac{2}{3}\right), \tag{1}$$

where $g_\parallel = g_\perp = 2.30$ [4].

$D$-parameter as a function of temperature or hydrostatic pressure was determined from the data obtained for the single crystal, whose trigonal axis was parallel to the direction of the magnetic field. Then the spectrum is maximally split into two lines corresponding to two allowed spin transitions ($\Delta S_z = \pm 1$). The widths of the lines are about 50 mT at ambient conditions. With increasing temperature, the distance between the two resonance lines decreases and then they merge. The value of the $D$-parameter decreases and reaches zero at 338 K when the resulting line width of two overlapping lines becomes minimal.

The results of the pressure measurements at three constant temperatures: 196 K, 273 K, and 350 K are shown in Fig. 1. The dependence of $D$ on pressure is linear. From the linear fit to the experimental data the value of the pressure
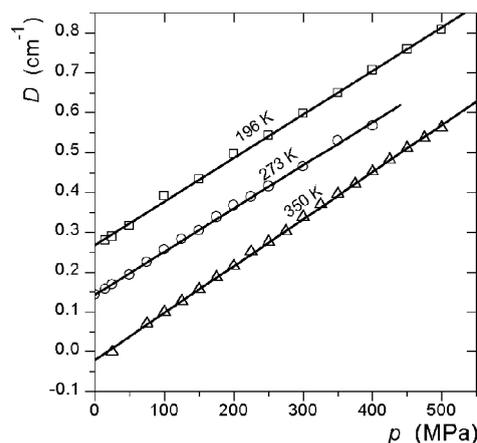
Fig. 1. The $D$-parameter of $NiSnCl_6 \cdot 6H_2O$ as a function of hydrostatic pressure for three constant temperatures.

coefficient $(\partial D/\partial p)_T$ equal to $(10.9 \pm 0.2) \times 10^{-4}$ $cm^{-1}/MPa$ below room temperature and $(11.8 \pm 0.1) \times 10^{-4}$ $cm^{-1}/MPa$ at 350 K is obtained. For the latter, the change in the sign of $D$ under the pressure of 25 MPa is observed.

The crystal powder measurements were carried out in the range of temperatures and pressures, in which the $D$-parameter is small and reaches zero i.e. between 300 and 390 K up to 160 MPa. A broad spectrum of $Ni^{2+}$ ions averaged over all orientations of the crystallites of the powder sample with respect to the direction of the steady magnetic field $\boldsymbol{B}$ is observed. When $D$ decreases, the peak-to-peak distance of the spectrum decreases and in the case of $D = 0$ we deal with one symmetric Lorentzian line with the minimal width. Such behaviour of the powder spectrum permits determination of the range of pressures and temperatures for which $D = 0$. The values are inserted in Fig. 2 and approximated by a
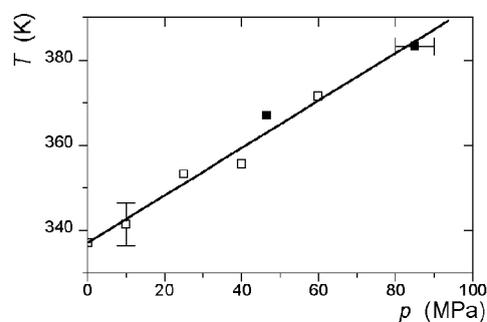


Fig. 2. The temperature versus pressure when $D = 0$. Open squares are the minima of the effective line width obtained from the constant pressure measurements; solid squares — from the constant temperatures.

linear plot using the least squares method. Thus, the following dependence of the temperature when $D = 0$ on hydrostatic pressure has been determined:

$$T_{D=0} = 337(2) + 0.56(4)p, \tag{2}$$

where brackets give the errors; $T$ and $p$ are expressed in K and MPa, respectively.

The dependence of the $D$-parameter on hydrostatic pressure at a constant temperature can be obtained if Eq. (1) is combined with the temperature dependence of $D$. From the differential of the function $D = D(p, T)$ the following expression for the pressure coefficient when $D = 0$ is found:

$$\left( \frac{\partial D}{\partial p} \right)_T = - \left( \frac{\partial D}{\partial T} \right)_p \left( \frac{\partial T}{\partial p} \right)_{D=0}. \tag{3}$$

This equation allows a determination of the pressure coefficient $(\partial D / \partial p)_T = (11.2 \pm 1.2) \times 10^{-4}$ cm$^{-1}$ MPa$^{-1}$, which is close to that obtained directly from the single crystal measurements.

## 3. Discussion

Let us compare the temperature and pressure changes in the $D$-parameter for NiSnCl$_6$·6H$_2$O with those obtained by Walsh [6] for NiSiF$_6$·6H$_2$O. For both compounds, the temperature variations of $D$ in the vicinity of room temperature are linear and the temperature coefficients, $(\partial D / \partial T)_p$, are similar [4] in spite of the opposite signs of $D$. The value of the pressure coefficient $(\partial D / \partial p)_T$ obtained in this work for nickel chlorostannate is about 30% larger than for nickel fluosilicate. This fact is related to a higher compressibility of the NiSnCl$_6$·6H$_2$O lattice.

As it was shown by Walsh [6], the $D$-parameter is independent of the volume of the crystal within the experimental error, but it is considerably sensitive to the unit cell shape. The changes $D$ under pressure are mainly caused by deformations of the water octahedron, its elongation or flattening along the threefold axis of symmetry. This deformation leads mainly to changes in the polar angle $\alpha$ of the octahedron; the change in the Ni–ligand distance is neglected. The deviation of $\alpha$ from $\alpha_0 = 54°44'$ (the polar angle for the regular octahedron) causes the appearance of the trigonal component of the crystalline field acting on Ni$^{2+}$ ion and thus a non-zero $D$. For NiSiF$_6$·6H$_2$O the static, ionic model of the [Ni(H$_2$O)$_6$]$^{2+}$ octahedral complex leads to the following dependence [6]:

$$D = -50.4(\alpha - \alpha_0) \text{ cm}^{-1}.$$

In nickel fluosilicate the strong influence of temperature on $D$ under constant dimensions of the unit cell is observed, which means that dynamics of the water octahedron and all crystal lattice considerably participate in $D$. For these reasons we assume that the observed temperature and pressure dependence of $D$ is a complex function of the form: $D = D[T, \alpha(T, p)]$. Differentiating this expression we obtain

$$\left(\frac{\partial D}{\partial T}\right)_p = \left(\frac{\partial D}{\partial T}\right)_\alpha + \left(\frac{\partial D}{\partial \ln \alpha}\right)_T \left(\frac{\partial \ln \alpha}{\partial T}\right)_p, \tag{4a}$$

$$\left(\frac{\partial D}{\partial p}\right)_T = \left(\frac{\partial D}{\partial \ln \alpha}\right)_T \left(\frac{\partial \ln \alpha}{\partial p}\right)_T, \tag{4b}$$

where $(\partial \ln \alpha/\partial T)_p = \beta_\alpha$ and $(\partial \ln \alpha/\partial p)_T = \kappa_\alpha$ are the cell shape thermal expansion and compressibility coefficients, respectively. After elimination of $(\partial D/\partial \ln \alpha)_T$ from Eqs. (4) the following equation is obtained:

$$\left(\frac{\partial D}{\partial T}\right)_p - \left(\frac{\partial D}{\partial T}\right)_\alpha = \frac{\beta_\alpha}{\kappa_\alpha}\left(\frac{\partial D}{\partial p}\right)_T, \tag{5}$$

whose left side represents the contribution to the observed temperature changes of the $D$-parameter coming from the thermal expansion of the crystal lattice. In the calculations we omitted the dependence of $D$ on the metal–ligand distance, which because of small radial compressibility of the octahedron gives negligible contribution. Thus, the measurements under uniaxial stress are not needed. For $NiSiF_6 \cdot 6H_2O$ on the basis of Walsh data [6] the ratio $\beta_\alpha/\kappa_\alpha = 4.55$ MPa/K is obtained, but from our last more accurate data [10] this ratio is less and equals 2.71 MPa/K. From the last value and Eq. (5) we obtain that the contribution of the thermal expansion of the crystal equals $24 \times 10^{-1}$ cm$^{-1}$/K and the phonon contribution is $-39 \times 10^{-1}$ cm$^{-1}$/K. The rhombohedral unit cell of $NiSnCl_6 \cdot 6H_2O$ ($a = 0.709$ nm, $\alpha = 96.8°$ [1]) has larger dimensions than that of $NiSiF_6 \cdot 6H_2O$ ($a = 0.626$ nm, $\alpha = 96°6'$ [11]). Unfortunately, no experimental data on the thermal expansion and compressibility coefficients are known for nickel chlorostannate and so the exact calculation of the phonon and geometrical contributions to $D$ is not possible. Nevertheless, from the similar behaviour of the $D$-parameter as a function of temperature and pressure for both compounds we may suppose that the both contributions: phonon and geometrical, are in $NiSnCl_6 \cdot 6H_2O$ approximately the same. It suggests a similar molecular mechanism of the origin of the axial crystal-field splitting $D$ and its temperature and pressure changes in these two crystals.

## Acknowledgments

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