STAN-J 73-0242

Vol. A43 (1973) ACTA PHYSICA POLONICA No 3

With compliments
Poznań 19.09.1973 r.

INFLUENCE OF HIGH PRESSURE ON THE EPR SPECTRA OF TGFB:Cu^{2+} MONOCRYSTALS

By J. Stankowski, S. Waplak, A. Gałęzewski and M. Maćkowiak

Division of Radiospectroscopy, Institute of Physics, Polish Academy of Sciences, Poznań*

(Received April 11, 1972)

EPR pressure-dependent spectra of a four nuclei copper complex in a TGFB crystal in the range up to 12 kbar were investigated. It was found that the D and E values changed from 0.108 and 0.030 cm^{-1} at normal pressure to 0.072 and 0.020 cm^{-1} at 12 kbar, respectively. Similar changes have been also found when the temperature of the doped crystal was decreased. The changes of D and E are associated with a rotation of the NH_3 group. At temperatures below 100 K and under a pressure exceeding 8 kbar the crystal becomes rigid (clamped) hence, effects caused by the pressure are then proportional to the macroscopic compressibility of the crystal.

1. Introduction

Investigations concerning the influence of pressure on the dielectric properties of TGS had been carried out in different laboratories, but the most interesting first results in the range up to 10 kbar were acquired by Jona and Shirane [1]. Netesova and Leonidova [2] measured the dependence of the Curie Point of TGS as a function of temperature in the range up to 20 kbar. For TGFB crystals also a shift of the Curie Point with changing applied pressure [3] (up to 8 kbar) was found. New ferroelectric phases in TGS crystals were determined in the course of pressure investigations [4].

The work presented here is a preliminary study of the influence of hydrostatic pressure on the EPR spectrum of copper-doped glycine fluoroberylate. This copper complex was described earlier by Stankowski and Maćkowiak [5]. Its theoretical model is now being considered by Maćkowiak and Kurzyński [6].

2. Apparatus for pressure investigations of EPR spectra

The apparatus consists of a pressure multiplicator made from beryllium copper and achieves pressure increases up to about 15 kbar (Fig. 1). A manual pump compresses the oil by means of the large piston in the multiplicator to value of 1 kbar. Thanks to the

* Address: Zakład Radiospektroskopii, Instytut Fizyki PAN, Mielżyńskiego 27/29, 61–725 Poznań, Poland.

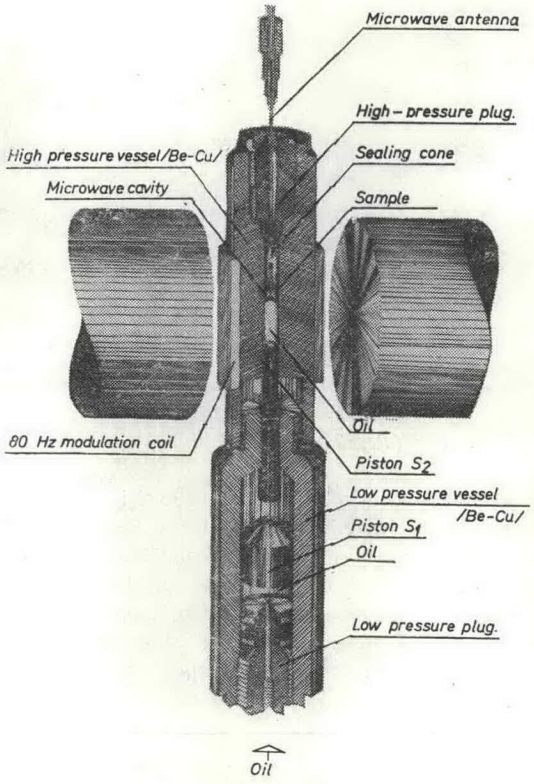


Fig. 1. High-pressure set-up for EPR measurements

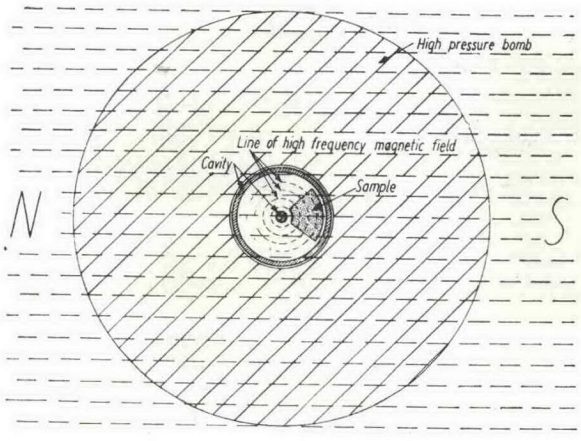


Fig. 2. Configuration of the high-frequency field in the resonator and the position of the crystal in the external magnetic field

ratio of surfaces $S_1 : S_2$ of the two pistons in the multiplicator a pressure of 13 kbar was obtained in the working volume of the chamber. The ratio $S_1 : S_2 = 15$ was not equal to the pressure ratio and had a value of 14 in the range to 7 kbar and 13 at 10 kbar. This was mainly caused by the friction of the pistons. The pressure chamber had the following dimensions: inner diameter — 9 mm, outside diameter — 55 mm, working length — 60 mm. In the EPR experiments a concentric resonator capacitor coupled with an antenna was used. The antenna consists of a cone-shaped washer mounted on pyrofilite. The construction was based on an idea earlier proposed by Walsh and Bloembergen [9, 10] and is very useful when EPR signals are strong enough. A drawback of this chamber is the change in its resonance frequency (about 9%) when under pressure. This change is caused by an increase in the electric permittivity of the paraffin oil. Furthermore, increased pressure caused changes in the coupling between the resonator and the antenna, and investigations of EPR signals became more troublesome.

The EPR experiments were carried out using a Japanese JES-3BX spectrometer with magnetic field modulation at 80 Hz accomplished by means of special coils placed outside the pressure chamber. The multiplicator was firmly attached to the electromagnet, thus eliminating undesirable vibrations of the total chamber. Figure 2 schematically presents the high frequency field pattern inside the resonator and the position of the crystal in the external magnetic field.

3. *EPR spectrum of the* TGFB : Cu^{2+} *crystal*

The four-center complex is composed of plane glycine complexes, investigated earlier by Loesche and Windsch [7] and Stankowski [8]. Coupling between isolated glycine complexes yield a magnetic center exhibiting an effective spin values of $S = 2$. In the EPR spectrum four lines associated to the following quantum transitions were found: $M_s = \pm 2 \leftrightarrow M_s = \pm 1$, $M_s = 0 \leftrightarrow M_s = \pm 1$ (allowed lines) and $M_s = 1 \leftrightarrow M_s = -1$, $M_s = -2 \leftrightarrow M_s = 0$ (forbidden lines). In describing the spectrum the spin Hamiltonian given in [5] and [6] was used and the following results at room temperatures were obtained:

$$\mathcal{H} = -\sqrt{\tfrac{2}{3}}\, D P_0^2(\vec{S}) - E[P_2^2(\vec{S}) + P_{-2}^2(\vec{S})] + a\{\sqrt{\tfrac{14}{45}}\, P_0^4(\vec{S}) + \tfrac{1}{3}[P_4^4(\vec{S}) + P_{-4}^4(\vec{S})]\} +$$

$$+ b\{-5\sqrt{\tfrac{14}{45}}\, P_0^4(\vec{S}) + \tfrac{7}{3}[P_4^4(\vec{S}) + P_{-4}^4(\vec{S})]\} + \frac{\sqrt{7}}{3} c[P_2^4(\vec{S}) + P_{-2}^4(\vec{S})] + \beta \cdot \vec{B} \cdot \hat{g} \cdot \vec{S} \quad (1)$$

$D = 0.108\ \mathrm{cm}^{-1}$, $E = 0.030\ \mathrm{cm}^{-1}$, $a = -0.003\ \mathrm{cm}^{-1}$, $b = 0$, $c = 0.009\ \mathrm{cm}^{-1}$, $g_x^{(D)} = 2.08$, $g_y^{(D)} = 2.15$, $g_z^{(D)} = 2.12$ where $g_i^{(D)}$ are the main g values calculated in a system associated with the main directions of the D tensor. These lines, which have their origin in the $M_s = 0 \leftrightarrow M_s = \pm 1$ transitions, have maximum amplitude and therefore were further investigated at higher pressure, where the sensitivity of detection EPR signal drops by 20 db as compared with measurements with an open resonator.

EPR investigations at room temperature were carried out in the main direction of the D tensor for one out of two aggregates. Table I presents the resonance field values B_{res}

and the resonator frequency f obtained as function of pressure. The last column indicates values of the resonance field reduced to a constant frequency of 8.986 GHz.

Assuming the rhombic crystal field parameter does not change under hydrostatic pressure and taking the results of Table I, a plot of the dependence of D *versus* pressure was drawn (Fig. 3). The change in the D value is seen to be 33.0%.

TABLE I

p(kbar)	f(GHz)	$B_{res}(T)$	$B_{res}(T)$ reduced to 8.98 GHz
0	9.13	0.4525	0.4475
1.50	9.03	0.4410	0.4393
3.00	8.97	0.4210	0.4213
4.50	8.91	0.4100	0.4123
7.50	8.86	0.3925	0.3965
12.90	8.82	0.3850	0.3905

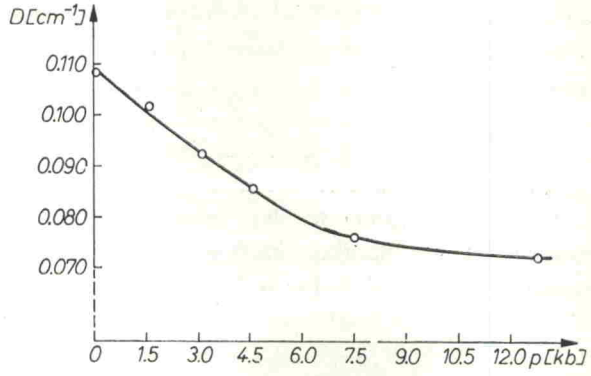


Fig. 3. Parameter D of the four-ion copper aggregate of effective spin $S = 2$ in TGFB *versus* hydrostatic pressure

4. *Discussion*

The EPR spectra of isolated plane copper complexes, as well as those of four copper aggregates in triglycine fluoroberylate, were investigated as function of pressure. The spectrum of isolated complexes practically did not depend on pressure. Benedek [10] suggests that the change of the spectroscopy splitting factor g is a function of the distance between ligand taken in the fifth power:

$$\frac{\partial \ln (g - g_0)}{\partial \ln R} = \frac{\partial \ln D_q}{\partial \ln R} = 5 \tag{2}$$

which gives for the compressibility of MgO a relative change $\frac{1}{\Delta g}\frac{d(\Delta g)}{dp}$ for Mn^{2+} of the order of 10^{-6} kg^{-1} cm^2. In our case the measurement accuracy was by one order of magni-

tude lower, which resulted in a very large line-width of the hyperfine structure. Successful detection of the pressure effect in the EPR spectrum of an isolated copper complex seems to be possible if a ^{63}Cu-doped deuterized crystal is used.

On the other hand, a very large pressure effect in the EPR spectra of four center copper aggregate was found. The results obtained for isolated complexes imply that the total pressure effect is caused by a change in parameters D and E, the g_x, g_y and g_z remaining constant. The ratio $\frac{1}{D}\frac{dD}{dp}$ calculated at low pressure has a value of 4.51×10^{-5} bar^{-1}, and approaches zero at higher pressure. In the course of our experiments we noticed the crystal field parameter changes as the fifth power of the distance between ligands, which can be associated with the macroscopic compressibility in the following way:

$$\frac{(D_q)_p}{(D_q)_o} = \left(\frac{\varrho_p}{\varrho_o}\right)^{5/3} \tag{3}$$

where parameters with the subscripts p and o represent orbital splitting values D_q and density ϱ of the crystal under pressure and when the pressure was removed, respectively. The macroscopic compressibility, though similar to that of the isolated complex, yields effects immeasurable by means of our apparatus.

In explaining the pressure effects it was assumed that the spin exchange takes place through the BeF_4 and the glycine, the latter denoted by Hoshino and Pepinsky [11] as glycine I. This model is supported by the fact that in the isomorphic TGS crystal there is no creation of aggregates hence, the Gly II and Gly III do not take part in the spin exchange phenomena. We have also investigated the influence of hydrostatic pressure (in the range up to 12 kbar) on EPR spectra of $Cu(CH_3COO)_2 \cdot H_2O$, and no detectable changes in the spin Hamiltonian parameters were found [12]. In this crystal the Cu^{2+} ions are coupled into pairs by antiferromagnetic interaction, characterized by an exchange energy of $J = 300$ cm^{-1}, and the EPR spectrum can be described by means of an effective

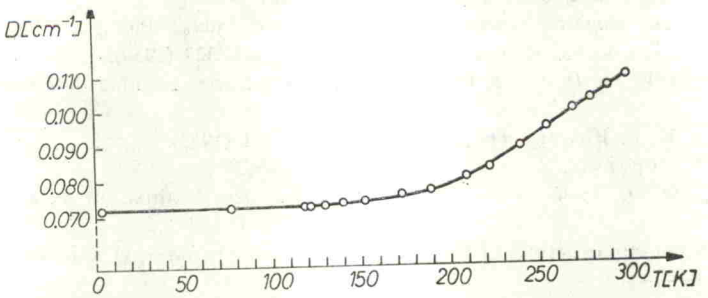


Fig. 4. Parameter D of the four-ion copper aggregate with $S = 2$ in TGFB *versus* temperature

spin Hamiltonian for $S = 1$ [13]. The spin Hamiltonian parameters are practically temperature-independent.

A pressure of 10 kbar is too low to directly influence the exchange interaction through a change in the overlapping of atomic orbitals. Changes under hydrostatic pressure of

10 kbar can be realized indirectly when the crystal lattice contains rotating groups which, in the case of TGFB, is fully satisfied because the NH_3 rotates at higher temperatures. The large change in the D value (Fig. 3) is associated with hindered rotation of the NH_3 group in the glycine molecule. This conclusion is also supported by the fact that temperature as well pressure characteristics of the D parameter are similar. Figure 4 shows that the D value becomes stationary and equal 0.072 cm^{-1} at a temperature of about 110 K and remains constant down to liquid helium temperatures[1]. This D value is the lowest one obtained under a pressure of 12 kbar. Thanks to the investigations of Blinc [14] and Dezor [15] we know that at about 110 K the hindered rotation becomes suppressed and at lower temperatures the crystal is rigid. For such a crystal the changes in D values depend on macroscopic compressibility, which gives the effect measured by the present authors. Thus, the large change in D value caused by temperature variations or by hydrostatic pressure depends on the dynamic phase of the TGFB crystal, *i. e.*, when the NH_3 rotations are present. The influence of internal rotation on the dielectric properties of TGS and TGFB crystals will be presented in a separated paper [16].

The authors appreciate the technical support of Mr Bujnowski in preparing some elements of the pressure apparatus and would like to thank Dr J. Stankowska and Dr B. Hilczerowa for growing the copper-doped crystals.

REFERENCES

[1] F. Jona, G. Shirane, *Phys. Rev.*, **117**, 139 (1960).
[2] N. P. Netesova, G. G. Leonidova, *Fiz. Tverdogo Tela*, **11**, 819 (1969).
[3] V. P. Mylov, I. N. Polandov, B. A. Strukov, *Fiz. Tverdogo Tela*, **9**, 3012 (1967).
[4] I. N. Polandov, V. P. Mylov, B. R. Churagulov, *Dokl. Akad. Nauk SSSR*, **178**, 1293 (1968).
[5] J. Stankowski, M. Maćkowiak, *Phys. Status Solidi*, (6) **51**, 449 (1972).
[6] M. Maćkowiak, M. Kurzyński, *Phys. Status Solidi*, (6) **51**, 841 (1972).
[7] A. Lösche, W. Windsch, *Phys. Status Solidi*, **11**, K55 (1965).
[8] J. Stankowski, *Proc. Int. Meeting on Ferroelectricity*, Prague 1966; *Acta Phys Polon.*, **33**, 387 (1968).
[9] W. M. Walsh, N. B. Bloembergen, *Phys. Rev.*, **107**, 904 (1957).
[10] G. B. Benedek, *Magnetic Resonance at High Pressure*, Intersc. Publ., J. Wiley 1963.
[11] S. Hoshino, Y. Okaya, R. Pepinsky, *Phys. Rev.*, **115**, 323 (1959).
[12] M. Maćkowiak, *Ph. D. Thesis*, Polish Academy of Sciences, Institute of Physics, Poznań 1972, in Polish.
[13] B. Bleaney, K. B. Bowers, *Proc. Roy. Soc.*, **A214**, 451 (1952).
[14] R. Blinc, J. Zupancic, *J. Phys. Chem. Solids*, **24** (1963).
[15] A. Dezor, *Ph. D. Thesis*, Polish Academy of Sciences, Institute of Physics, Poznań 1970, in Polish.
[16] J. Stankowski, A. Gałęzewski, S. Waplak, U. Gruszczyńska, H. Gierszal (in preparation).

[1] Thanks are due to Professor K. Leibler and to Mr Wilamowski for the results on EPR spectra taken at liquid helium temperature.