THE ELECTRON PARAMAGNETIC RESONANCE IN REDUCED BaTiO₃ CRYSTALS

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The electron-spin resonance of reduced BaTiO₃ crystals, which was studied by Z. Šroubek and K. Ždánský [Czech. J. Phys. B 13 (1963), 309], is interpreted as the resonance of the Ti³⁺ ion. The facts which favour this interpretation are discussed. The distortion of the oxygen ions surrounding the Ti³⁺ ion has been taken into account in order to explain the measured electron paramagnetic resonance spectrum. Considering the crystal-field model of C₄ᵥ point-group symmetry, the Stark energy-level separations of the Ti³⁺ ion and the values of the g factors are calculated.

1. INTRODUCTION

The optical properties of reduced non-stoichiometric BaTiO₃ crystals have been studied by Coufová and Arend [1] and theoretically treated by Dvořák [2]. To explain their results they have suggested a model of one electron captured on an oxygen vacancy. The exact localizations of the electron can be solved by electron paramagnetic resonance (EPR) studies.

The EPR in reduced non-stoichiometric BaTiO₃ crystals has been studied by Šroubek and Ždánský [3]. The preparation of the samples and the chemical processes during the hydrogen reduction have been discussed by Arend, Coufová and Novák [4]; all these samples were grown from a potassium fluoride flux. The resonance was observed in the crystals reduced for at least two minutes, but less than four hours, at 700–900°C in a hydrogen atmosphere. No resonance was found in the crystals reduced for more than four hours. The reduction in the argon atmosphere does not cause any resonance. The Fe³⁺ ions act as killers and in the crystals with a large amount of Fe³⁺ ions no EPR of the type observed by Šroubek and Ždánský [3] can be detected.

The purpose of this paper is to give a new interpretation of the measured resonance [3], which is in agreement with experimental facts. It will be shown that the most consistent model of the centre is an electron trapped on a Ti⁴⁺ ion, which has an oxygen vacancy as its nearest neighbour.

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2. EXPERIMENTAL PROCEDURE

The resonance was found at 78°K. When the temperature is increased the resonance curve broadens and vanishes. An EPR x-range spectrometer was used. The $g$ factors were estimated as:

$$g_{\perp} = 1.930 \pm 0.004$$
$$g_{\parallel} = 1.916 \pm 0.006$$

The paramagnetic centres have three magnetic non-equivalent positions with the principal axes pointing in the direction of the crystal axes. The line width of the $g_{\perp}$ absorption curve is twice as large as the $g_{\parallel}$ curve. The measurements performed at 4°K do not show any substantial narrowing of the resonance line. Therefore the line width is probably due to the inhomogeneity of the crystal. Also no remarkable saturation of the absorption line was found up to 1 mW of microwave power.

3. INTERPRETATION OF THE EPR SPECTRUM

The ions $O^{2-}$ are assumed to have nearly $O_4$ symmetry round the ion $Ti^{4+}$ in the unreduced crystals. By the hydrogen reduction of the crystals a vacancy appears at the position of one ion $O^{2-}$ and at the same time electrons are set free in the crystal. One electron can be captured by the oxygen vacancy and gives rise to the observed EPR signal. The exact localization of the electron is the subject of discussion.

In order to explain the measured $g$ factors we shall consider two most probable positions of the captured electron.

1. The electron is localized in the oxygen vacancy (an F-centre).

2. The electron is localized on a $Ti^{4+}$ ion next to the oxygen vacancy, which leads to the appearance of the $Ti^{3+}$ ion.

The measured spectrum in [3] was interpreted as the resonance of the F-centre. As was pointed out also in [3], the interpretation of the $g$ factor values on the framework of this model leads to serious troubles.

Assuming the second model, the observed $g$ factor values can be explained quite naturally, as will be shown below.

The deviations of the $g$ factors from the free electron value are according to Pryce [5] determined by electron virtual excitations. The high inhomogeneity of the crystal field broadens the excitation energy orbital levels. As the $\Delta g_{\perp}$ deviation is caused by the excitations between the ground and the lower excitation levels, and the $\Delta g_{\parallel}$ deviation between the ground and the higher level, the influence of the spread on the width of the resonance curves is more pronounced in the case of $g_{\perp}$ than in the case of $g_{\parallel}$. Therefore, the $g_{\perp}$ resonance curve will be broader than the $g_{\parallel}$ one, in accordance with our experimental results.