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LETTER TO THE EDITOR

Shift of the transition temperature in the growth bands of potassium dihydrogen phosphate monitored by electron paramagnetic resonance

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In a recent study using electron paramagnetic resonance (EPR) of potassium dihydrogen phosphate (KDP) samples from the so-called growth bands [1], EPR spectra of Cr^{3+} ions have been found to differ from those previously reported for regular samples (not in the growth-band region) [2]. The differences consist of slightly lower values for the $B_2^0 = D/3$ and $B_2^2 = E$ spin-Hamiltonian parameters, as well as for the ratio $3E/D$; moreover, the Z principal axis, defined as the axis exhibiting maximum splitting of the spectrum, is exchanged with the Y axis for Cr^{3+} in the bulk sample [1, 2].

These differences have been interpreted as being a consequence of a slight increase in the lattice parameters in the growth-band samples (GB samples) with respect to the regular samples (R samples). This explanation is supported by the measurement of the c parameter of samples taken from the growth-band region using synchrotron radiation plane-wave reflection topography [3], which shows a relative lattice parameter difference $\partial c/c$ of around 2×10^{-5} with respect to regular (inner) samples. Although the a and b parameters have not been measured in [3], the exchange of the Z and Y axes in the GB sample has been considered in [1] as being due to an increase in the a and b parameters that is even higher than that in the c parameter.

Such an increase in the lattice parameters should produce a detectable change in the temperature of the para–ferroelectric phase transition (T_c) of the GB samples with respect to the R samples, which is 122 K. In this work we have monitored the phase transition of KDP:Cr^{3+} for both types of samples (GB and R) by means of EPR, making use of the fact that when the crystal becomes ferroelectric upon cooling, each EPR line splits into two, owing to the presence of two ferroelectric domains [4]. In this way, we have detected an increase in T_c for the GB samples and we have interpreted this result according to the model presented in [5]. Also, the model allowed us to estimate the relative distortion of the KDP lattice across the c axis in the GB samples.

The experimental details of the crystal growth and orientation have been described in [1]. Samples of about 2 mm × 2 mm × 7 mm were cut from the growth-band region or the regular (inner) region; we also used samples that contained both types of region.

The EPR spectra were obtained using a Varian E-12 spectrometer in the X-band. The temperature of the sample was controlled by a Varian E-257 gas-flow temperature controller that was carefully calibrated in order to obtain an accuracy and stability of

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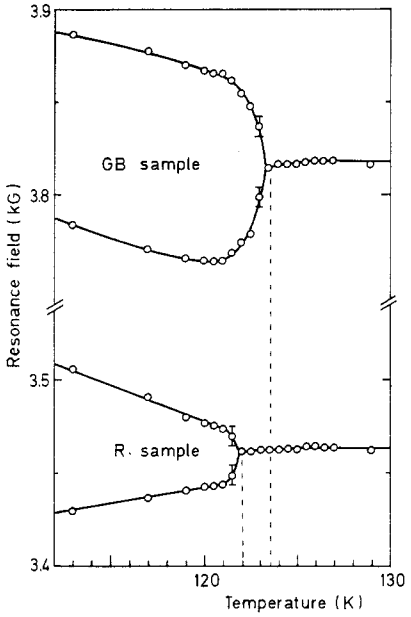

Figure 1. Splitting of the EPR lines in the phase transition (see text for details) for regular (lower part) and growth-band (upper part) samples of KDP: Cr^{3+}.

temperature in the sample of better than 0.5 K. The microwave frequency and absolute magnetic field were measured with a Hewlett–Packard frequency meter (model 5342 A) and a Bruker NMR gaussmeter (model ER 035 M) respectively.

In order neatly to observe the splitting of the EPR lines, we have chosen the line that is at about 2897 G in the R samples and at about 3939 G in the GB samples when $\boldsymbol{H}$ is parallel to the crystallographic a axis. This line corresponds to four defects among the eight equivalent defects associated with Cr^{3+} due to the KDP lattice symmetry [1, 2]. The samples were first oriented with $\boldsymbol{H}$ parallel to the a axis; next they were rotated by about 5° around the c axis and the waveguide of the spectrometer was tilted to split the line completely into four. When the sample becomes ferroelectric upon cooling, each line splits *again* into two, owing to the two ferroelectric domains [4].

Figure 1 shows that behaviour for a R sample (lower part) and a GB sample (upper part). It is observed that the R sample experiences the splitting at the normal $T_c = 122$ K, whereas in the GB sample the splitting takes place at 123.5 K. Therefore we conclude that the GB region of KDP presents a shift in the T_c up to 123.5 K. It must be pointed out that the result presented in figure 1 does not depend on the particular sample but only on the region of the crystal. In particular, a sample containing both regions, and therefore showing both EPR spectra, gives the same result as above.

According to [5], KDP and its isomorph can be adequately described by a simple two-sublattice model in order to describe the phase change whose transition temperature can be expressed as

$$T_c = [(\alpha + \beta)/4](N\mu^2/k). \tag{1}$$

Here N is the number of dipoles per unit volume, μ the electric dipole moment and k the Boltzmann constant. On the other hand, α and β are the coefficients relating the local effective field acting on unit dipoles at points in sublattices A and B, respectively, to the sublattice polarisations per unit volume, P_A and P_B, i.e.

$$(E_{\text{eff}})_A = E + \alpha P_A + \beta P_B \tag{2}$$

$$(E_{\text{eff}})_B = E + \beta P_A + \alpha P_B \tag{3}$$

where E is the external field. As was shown in [5], α and β depend on the tetragonality $(c/a - 1)$ of the lattice; thus it is possible to give the expression

$$\alpha + \beta = (\tilde{\alpha} + \tilde{\beta})(c/a - 1) \tag{4}$$

where $\tilde{\alpha}$ and $\tilde{\beta}$ are constants for each family of isomorphous materials.

Therefore, from equations (1) and (4) we obtain

$$T_c \propto (c/a - 1) \tag{5}$$

and, taking increments, we get

$$\partial T_c/T_c = (\partial C\, a - c\, \partial a)/a(c - a). \tag{6}$$

Substituting in the values for the lattice parameters [6] $a = 7.4529$ Å, $c = 6.974$ Å and the increment of the c parameter given in [3], $\partial c/c = 2 \times 10^{-5}$ for the GB samples, we obtain a relative increment for the a parameter $\partial a/a \simeq 9 \times 10^{-4}$, which is considerably higher than that along the c axis, and which is in agreement with the interpretation of the EPR spectra measured at room temperature given in [1].

Thus, according to this model, the increase in the a parameter overcompensates the increase in the c parameter, resulting in a net increase in the transition temperature; this, in spite of the fact that the dipole–dipole distance is larger in the GB sample than in the R sample.

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