Cu2+ in NaF: EPR study of a dynamic center

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Abstract
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Reference

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Cu$^{2+}$ IN NaF : EPR STUDY OF A DYNAMIC CENTER

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An EPR study has been carried out on a Cu$^{2+}$ center in NaF single crystals (with 2 % mole of copper) from 1.6 K - 150 K. The symmetry of the EPR spectra is triclinic at 1.6 K, monoclinic at 4.2 K, tetragonal at T > 40 K. No hyperfine structure has been observed. Models which include both the Jahn-Teller effect and a low symmetry crystal field are proposed.

1. Introduction

Cu$^{2+}$ is a well-known model Jahn-Teller system which has been investigated in the past in a number of cubic or trigonal hosts, as for instance in several alkali halides. In particular a copper centre of orthorhombic symmetry was observed by Kuwabara$^1$ in NaF. His experimental results seem far from being complete as he published data only around 78 K. On the contrary, detailed results on Cu$^{2+}$ in NaCl have been published$^2$. This system exhibits a strong Jahn-Teller effect with a tetragonal EPR spectrum below approximately 95 K which becomes motional ly averaged above this temperature.

It seemed to us worthwhile to study in some detail the copper (2+) ion in NaF in order to obtain a more complete picture regarding the possible action of the Jahn-Teller effect in this system.

It turned out that it is quite difficult to introduce copper into NaF and, depending on the method of preparation, one obtains rather different results. In particular, we have not succeeded in reproducing the centre published by Kuwabaral. But, we have been able to create two other ones in a reproducible manner. This letter presents experimental EPR results about one of them.

2. Sample Preparation

As this part of study was not totally trivial, we feel justified to report a few facts about sample preparation.

Most of the crystals were grown by Bridgman method. Water-free powders of NaF and CuF$_2$ were introduced into a carbon crucible and gently heated (T ≤ 150°C) under high vacuum in the crystal growth furnace. A liquid nitrogen trap connected to the furnace ensured a low partial pressure of H$_2$O, O$_2$. About 24 hours later, the crystal was then grown, in a helium atmosphere, with a char-coal trap (cooled to 78 K) connected to the vessel.

Crystals containing initial dopant concentrations ranging from 0.04 to 2 mole % were grown. As the distribution of the copper ions in the crystals was always found to be inhomogeneous, we use this nominal dopant concentration to characterize the samples.

The growth velocity and the effective copper concentration in the crystal turned out to be closely related.

Usually the as-grown crystals consisted of a pure NaF body and a metallic copper deposit either on its surface or as an inclusion in the interior. Our experiments showed that the quantity of copper which is microscopically dissolved depends very critically on the presence (or absence) of oxygen and (OH$^-$) groups during the crystal growth. The following chemical reaction of the copper in the presence of some oxygen traces seems to occur:

1) n ( 2 CuF$_2$ $\rightarrow$ 2 CuF + F$_2$ )
   (probably slow)  \hspace{1cm} \rightarrow \hspace{1cm}
   metallic copper clusters + n F$_2$

2) ( NaF + CuF$_2$ )melt + oxygen
   NaF + metallic copper

When oxygen or (OH$^-$) groups are present, equation (2) seems predominant. The details were not investigated but the final products are: pure NaF crystal and metallic copper.

Indeed, only the one of our growth procedures which we described above gave satisfactory and rather reproducible doped crystals.

Some experiments were performed to introduce copper by diffusion in pure NaF crystals, but without success. Typically, CuF$_2$, CuI, CuO, Cu$_2$O or Cu were introduced as powders into a nickel or a quartz tube in the presence of a
pure NaF crystal under an inert atmosphere or under NH₄F.HF or Cl₂ atmosphere. The sealed tube was then heated to 600°C. No copper centers were observed in those crystals after this treatment.

Suitable crystals grown by the Bridgman method contain a useable concentration of Cu²⁺ without any further treatment (such as X-irradiation or annealing).

A few doped samples were X-rayed at room temperature and also at 78 K. No changes were observed in the EPR experiments with regard to the copper signals.

Electron Micro-Probe measurements reveal that aggregation of copper occurs in part of the as-grown crystals. It may be remarked that the crystal growth process mentioned above could be a suitable method for the production of metallic micro-clusters.

3. Experimental Results

The EPR spectra were recorded on a Varian 9 GHz spectrometer and also a home-built 36 GHz apparatus.

Generally the present center is found in heavily doped crystals (1-2 % mole). The as-grown crystal axes at 78 K the spectra shown in figure 1. The multiplicity of the spectrum (recorded in (110) and (001) type planes) indicates that the center has tetragonal symmetry. The experimental g-values at 78 K are:

\[ g_{11} = 2.458 \pm 0.005 \]
\[ g_{1} = 2.105 \pm 0.005 \]

The EPR lines have a width which depends on the angle and ranges from 100 to 150 Gauss. No resolved hyperfine structure is observed.

This spectrum is a motionally averaged one. Indeed, when the crystal is cooled to 1.6 K one observes at X-band frequencies the EPR spectra shown in figure 2. As can be seen from this figure, this spectrum is of lower than tetragonal - indeed triclinic - symmetry.

A detailed study of the angular dependence of the resonance spectrum was realized with H rotating in (001) and (110) type planes. The analysis based on the angular plots obtained in the three mutually orthogonal (001) planes was performed in the usual way and the results are depicted in figure 3.

The principal g-values and the Euler's angles specifying the axes have the following values:

\[ g_{11} = 2.0124 \pm 0.005 \]
\[ g_{22} = 2.1328 \pm 0.005 \]
\[ g_{33} = 2.5139 \pm 0.005 \]

with the following Euler's angles:

\[ \alpha = 9.4^\circ \pm 0.5^\circ \]
\[ \beta = 16.8^\circ \pm 0.5^\circ \]
\[ \gamma = 6.7^\circ \pm 0.5^\circ \]

(The convention of Whittaker applies, definition of the angles according to Tinkham⁴)

The EPR lines are large and have line...
4. Discussion

The following facts suggest that this Cu$^{2+}$ center involves modifications of its neighborhood. Firstly, we have identified a second Cu$^{2+}$ center of tetragonal symmetry at low temperature which seems to be surrounded by an unaltered octahedral environment and it seems to involve the Jahn-Teller effect.

The presently reported center has triclinic symmetry at very low temperature. The presence of a vacancy in the first neighborhood is unlikely since this geometry would produce a stable tetragonal center due to a strong ligand field. On the other hand, a vacancy in the second neighborhood gives rise to a C$_2$V or C$_s$ site symmetry of the Cu$^{2+}$ ion. This comparatively weak ligand field in conjunction with an $E_g \otimes (E_g + T_{lu})$ Jahn-Teller effect might create an off-center deformation leading to the observed very low symmetry of the copper resonance. Such a model has the further advantage to fulfill local neutrality.

A second possible model, depicted in figure 4, can not be excluded at present. It contains a sodium vacancy in a [011] direction and a Cu$^+$ impurity substituting a Na$^+$ ion located in a [012] direction, both occupying a second neighborhood position. Again, the low symmetry crystal field in conjunction with an $E_g \otimes (E_g + T_{lu})$ Jahn-Teller effect is responsible for the observed structure of the adiabatic ground state potential.

The temperature dependence of the spectrum was studied at Ka-band with H being oriented along a C$_4$ crystal axis. The triclinic spectrum (figure 2) consists of three lines (with g-values: $g_x = 2.057 \pm 0.002$, $g_y = 2.143 \pm 0.005$, $g_z = 2.489 \pm 0.001$) along this direction. When the temperature is increased from the initial 1.6 K the splitting between the lines corresponding to $g_x$ and $g_y$ decreases steadily. Between 1.6 K and 40 K, an exponential law describes the temperature variation of this splitting. The parameters of this empirical fit are:

$$\Delta g = (g_y - g_x) = a \exp(-0.7 \cdot T)$$

where $a = 0.11$

The whole process is reversible.

Several stress experiments were performed on these systems at 1.6 K and 4.2 K. Samples ($\approx 2$ % mole doped) were selected which gave a good signal to noise ratio. Yet, no repopulation effects were observed for $P \leq 500$ kg/cm$^2$.

Moreover, it was impossible to saturate this center. Our experimental setup did not yield a sufficient microwave magnetic field at the sample ($P < 200$ mW, $Q \approx 5000$) at $T > 1.6$ K.
As no motional averaging of the tetragonal "high temperature" spectrum is observed, one can conclude that the tetragonal deformations of this potential are deep. The low symmetry crystal field effects generate "secondary minima" which are rather shallow with respect to those of tetragonal deformation. When the temperature is raised, effective motional averaging occurs between the different "secondary minima". This is indicated by the large linewidths which hide any hyperfine structure. It is obvious that any possible model must comply with the fact that the Jahn-Teller effect and crystal field effects compete in this system.

More work needs to be done on this system.

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