Electron Paramagnetic Resonance of Sc$^{3+}$-Stabilized CO$_3^-$ Molecule-Ion in Natural Calcite

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Abstract. Electron paramagnetic resonance (EPR) spectra of CO$_3^-$ molecule-ions stabilized by Sc$^{3+}$ in natural calcite were identified and studied at X-band frequencies and room temperature. The principal values of the g-tensor ($g_{xx}=1.9997$, $g_{yy}=2.0030$, $g_{zz}=1.9972$) and the direction cosines of the g and A tensors for CO$_3^-$-Sc$^{3+}$ center were found to be close to that for the well-known CO$_3^-$-Y$^{3+}$ center. A quantitative comparison of different impurity contents in calcite samples and analysis of the intensities of forbidden transitions were used to identify Sc$^{3+}$. An estimation of the unpaired electron spin density on the nuclei of paramagnetic centers confirms that both centers, CO$_3^-$-Sc$^{3+}$ and CO$_3^-$-Y$^{3+}$, have the same nature.

Introduction

Calcite has been a subject of numerous EPR studies (see, for example, references in Marfunin’s book (1979) and review of Poole et al. (1977)). It is noteworthy that calcite is a host, highly suited for studying EPR spectra of magnetic centers, due to its high degree of crystalline perfection and almost complete absence of nuclear magnetic moments. During the course of a systematic EPR investigation of paramagnetic defect centers in single crystals of natural calcite (Bershov 1970; Bershov et al. 1970; Mineyeva and Bershov 1969; Mineyeva et al. 1992), a new electron center with octet hyperfine structure was discovered. The calcite samples used in this investigation contain also well-identified CO$_3^-$-Y$^{3+}$ centers (Marshall et al. 1968). Similar behavior of both centers permits one to suggest that the new center is a CO$_3^-$ molecule-ion with M$^{3+}$ charge compensator, most likely Sc$^{3+}$, being a diamagnetic ion with nuclear spin $I=7/2$ of about 100% natural abundance. This center may be designated as CO$_3^-$-Sc$^{3+}$.

The purpose of this paper is twofold: (i) to determine accurately the spin-Hamiltonian parameters for the new center at room temperature and to compare them with the same parameters for the well known center CO$_3^-$-Y$^{3+}$, and (ii) to prove that the charge compensator for the new center is really Sc$^{3+}$.

Experimental

Three samples of transparent colorless natural single crystals of calcite were taken for investigation. In accordance with chemical analysis and laser microanalysis they contain as impurities (in wt. %): Mg-(0.001-0.1), Si-(0.01-0.05), Al-(0.03-0.1), Fe-(0.001-0.005), Cu-0.001, Y-0.003, Ni-trace amount. In one sample microinclusions with higher contents of Mn, V, Cu, Zn, Ti, Mg, Si, Al, Fe, Sr were discovered. EPR measurements were performed on samples of arbitrary shape.

Most of the EPR absorption data were recorded on a commercial RE-1306 spectrometer (USSR), some using a model Varian E-115, both operating at X-band frequencies and room temperature. The complexity of the EPR spectra of the new center required a special design of the crystal rotating device. The single crystals were aligned on a goniometer in the cavity of the spectrometer. They were rotated in the orthogonal laboratory system X, Y, Z with Y$\parallel$ a and Z$\parallel$ c. Precise alignment of the Zeeman field vector B with specific crystal directions was achieved because a degeneration of spectra was observed when the Zeeman field vector lay exactly along X, Y and Z axes. Spectra were measured in three mutually perpendicular planes every 10° and 2° over critical ranges. DPPH was used as a standard for determination of the microwave frequency. The spin-Hamiltonian parameters and the direction cosines were obtained by matrix diagonalization.

Results and Discussion

Figure 1 illustrates the EPR spectrum in calcite with high Y-content. Apart from the well-established centers PO$^0_4$ (Bershov 1970), CO$^2_2$ (Hughes and Soos 1970), CO$_3^-$-Y$^{3+}$ (Marsall et al. 1968) and Mn$^{2+}$ (Hurd et al. 1954) the pattern shows eight sufficiently intense allowed transitions with small forbidden doublets between them. Linewidths of allowed transitions are in the order of 0.1 Oe, thus making it possible to resolve the nonequivalent site components at most orientations.
The observed spectrum can be described by the spin-Hamiltonian

\[ H = \beta S g B + I_1 A_1 S - \beta N g S B + I_2 Q I_1 \]  

where \( S \) and \( I \) are the electron and nucleus spin operators, respectively, \( g, g_N, \beta, \beta_N \) and \( B \) are, respectively, spectroscopic splitting, nuclear \( g \)-tensor, the Bohr magneton, the nuclear magneton, and Zeeman field vector, while \( A \) and \( Q \) are the hyperfine interaction and quadrupole-coupling tensors, respectively. The repeated lower index is introduced so as to take account of interactions with various nuclei.

As a result of \( g \) and \( A \) tensors diagonalization, in accordance with the procedure described by Wertz and Bolton (1972), the principal values of the spectroscopic parameters and their orientation in the laboratory frame \( XYZ \) were received. They are given in Table 1. The two last terms in equn. (1) were omitted in these estimations because of their small magnitude.

The structure of calcite is based on the \( \text{R} \# \text{c} \) space group with two chemical formula units per primitive unit cell. The arbitrary direction is multiplied by the symmetry elements of point group \( 3m \), leading to twelve physically equivalent sites. These are interrelated by an inversion center. This reduces the number of sites, which are resolved by EPR, to six. When the Zeeman field vector lies in the \( ZX \) plane, which is the glide mirror plane, the degeneracy is still higher such that three spectra only can be observed. Twofold rotational symmetry about the \( Y \) axis and sixfold rotational symmetry about the \( Z \) axis leads to three spectra for \( B \parallel Y \) and to one spectrum for \( B \parallel Z \).

Figure 2 shows the upper hemi-sphere stereographic projection of the principal axes of \( g \) and \( A \) tensors for the three \( \text{CO}_3^\text{+} \rightarrow \text{M}^3\text{+} \) centers. The principal axes of \( g \) and \( A \) tensors of the other three centers pierce the lower hemi-sphere and are, therefore, not indicated in Fig. 2. For comparison, the principal axes of the \( g \)-tensor for the \( \text{CO}_3^\text{+} \rightarrow \text{Y}^3\text{+} \) center (Marshall et al. 1968) are also shown in Figure 2. It is obvious that the principal axes for the two centers, \( \text{CO}_3^\text{+} \rightarrow \text{Y}^\text{3+} \) and \( \text{CO}_3^\text{+} \rightarrow \text{M}^3\text{+} \), are very close to each other. Opposite to our case, Marshall et al. (1968) found that the \( \text{8}^9Y \) hyperfine tensor was diagonal in the calcite structure coordinate system at 77K. We have determined the spin Hamiltonian parameters for \( \text{CO}_3^\text{+} \rightarrow \text{Y}^\text{3+} \) center in calcite at room temperature and found that \( g \)-values and the principal axes of the \( g \)-tensor were close to that at 77K. But the \( \text{8}^9Y \) hyperfine tensor was not diagonal in the \( XYZ \) frame, the principal axes of \( \text{8}^9A \)-tensor occurring close to the principal axes of the \( g \)-tensor.

The observed spectral octet with equally spaced lines shows that the center includes an ion with a nuclear spin of \( 7/2 \) in about 100% abundance. From the analysis of the tables with EPR/ENDOR characteristics (Bruker Almanac 1991) one can find that only few elements have such parameters. These are \( ^{44}\text{Sc} \) with 100% abundance, \( ^{51}\text{V} \sim 99.75\%, \quad ^{59}\text{Co} \sim 100\%, \quad ^{133}\text{Cs} \sim 100\%, \quad ^{139}\text{La} \sim 100\% \).