Reinterpretation of temperature-induced dynamical behavior in the EPR spectrum of Rh^{2+} centers in AgCl

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Recent electron paramagnetic resonance (EPR) and electron-nuclear double-resonance research at 9.5 and 34 GHz have demonstrated that two types of $[\text{RhCl}_6]^{4-}$ complexes may coexist in AgCl crystals, depending on the crystal growth method and sample pretreatments. Based on these results, the temperature-induced changes to the EPR spectrum of Rh^{2+}-doped AgCl single crystals are convincingly explained by the difference in the dynamical behavior of the two complexes.

I. INTRODUCTION

Rh impurities in AgCl have been intensively studied in the past few decades because of their importance for the photographic industry.[1] Relatively small doping levels of Rh^{3+} tend to decrease the sensitivity and increase the contrast of photographic emulsions drastically. In order to understand this effect, attempts have been made to determine the ligand structure and charge compensation mechanisms of Rh complexes in AgCl and model systems, e.g., NaCl, by studying the trapped electron Rh^{2+} centers using electron paramagnetic resonance (EPR), electron-nuclear double-resonance (ENDOR), and optically detected magnetic resonance techniques.[2] It was found that local charge compensation is not mandatory for these complexes, which may partly explain the efficiency and depth of the Rh electron traps and/or the stability of the trapped electron centers.

The basic Rh^{2+}-related defect in melt-grown AgCl single crystals has been identified by Olm *et al.* as a Jahn-Teller elongated low-spin $[\text{RhCl}_6]^{4-}$ complex (Rh^{2+}, with a $4d^7\ ^2\text{A}_{1g}$ ground state, substituting for Ag$^+$), charge compensated by a Ag$^+$ vacancy in a next-nearest-neighbor position (on a $\langle 100 \rangle$ axis) in the plane perpendicular to the elongation axis.[3] This defect model is presented in Fig. 1(a). The presence of the vacancy was deduced from the rhombicity of the g tensor and several hyperfine and quadrupole tensors of interacting nuclei, determined from the ENDOR spectrum. The observation of temperature-induced changes to the EPR spectrum allowed to determine that the vacancy is located on the g_x axis of the complex ($g_x > g_y \gg g_z \approx g_e$). A recent Q-band ENDOR study presented a more direct way of determining the presence and position of this vacancy.[4] In the Q-band spectra, evidence was found for the existence of a second, nonlocally charge-compensated Rh^{2+} center, the model of which is shown in Fig. 1(b). In view of these results we reinterprete the dynamical behavior of the Rh^{2+} EPR spectra in AgCl single crystals.

II. INTERPRETATION OF THE TEMPERATURE DEPENDENCE OF THE EPR SPECTRUM IN TERMS OF A SINGLE $[\text{RhCl}_6]^{4-}$ COMPLEX

The temperature-induced changes to the EPR spectrum observed by Olm *et al.* can be summarized as follows. At the lowest temperatures ($T < 80$ K) the dominant Rh^{2+} complex is characterized by an orthorhombic g tensor and three distinct spectral components are observed when the magnetic field is, e.g., parallel to a $\langle 100 \rangle$ direction. When the temperature is raised above ~ 80 K, the g_y and g_z components and the superhyperfine structure on the g_x component of the spectrum gradually disappear. At temperatures above ~ 110 K, a new spectral feature appears which turns out to be the $g_\perp\ [\approx (g_y + g_z)/2]$ component of a tetragonal Rh^{2+} complex (with $g_\parallel = g_x$ of the low-temperature center). This completely reversible effect is typical of systems exhibiting a Jahn-Teller lowering of the symmetry and is explained by a thermal hopping of the elongation axis between the equivalent g_y and g_z axes of the complex. A similar effect has been observed for the dominant $[\text{RhCl}_6]^{4-}$ complex in melt-grown NaCl single crystals,[5] which is also charge compensated by a next-nearest-neighbor cation vacancy along the g_x axis and for other complexes, e.g., Ni$^+$-vacancy complexes in AgCl (with a $3d^9\ ^2\text{B}_1$ ground state).[6]

At temperatures near the ambient, the appearance of another EPR spectrum was reported, exhibiting cubic symmetry with $g_{\text{iso}} \approx (g_x + g_y + g_z)/3$. If the temperature was further raised to about 400 K, only this cubic center was detected. This effect has been interpreted by Olm *et al.* as the migra-
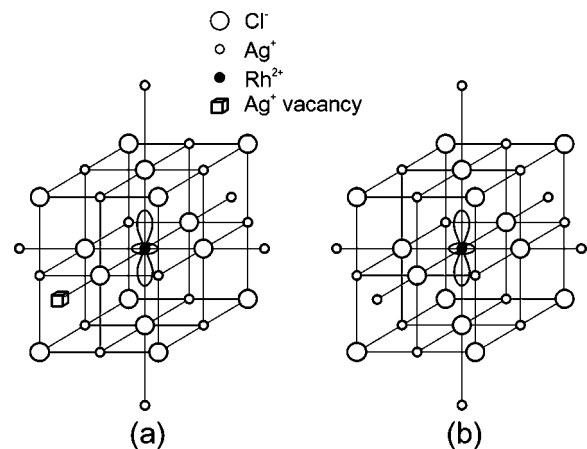

FIG. 1. Structural models for (a) the primary, locally charge-compensated and (b) the nonlocally charge-compensated Rh^{2+} complexes in AgCl.

tion of the vacancy away from the complex, resulting in a center with perfectly cubic symmetry. However, the conversion of the tetragonal to the cubic center appeared to be completely reversible, and in particular at temperatures below 80 K the orthorhombic center was found back in its original concentration after thermal anneals up to 400 K. This implies that the away diffusion of the vacancy should also be completely reversible, which does not seem to be *a priori* obvious. Moreover, for the similar Rh^{2+} complex in melt-grown NaCl and the orthorhombic Ni^+ center in AgCl, no similar high-temperature cubic variants have been found. The latter effect thus calls for an alternative explanation, which is given in the following section.

III. EVIDENCE FOR THE EXISTENCE OF A NONLOCALLY CHARGE-COMPENSATED $[RhCl_6]^{4-}$ DEFECT IN AgCl AND REINTERPRETATION OF THE TEMPERATURE DEPENDENCE OF THE EPR SPECTRUM

It has been demonstrated with Q-band EPR and ENDOR that the $[RhCl_6]^{4-}$ complex formed in AgCl emulsion microcrystals through irradiation of the Rh^{3+}-doped powders is fundamentally different from the dominant Rh^{2+} complex in melt-grown AgCl single crystals.[7] Following a comparison of the Q-band EPR spectra of irradiated and heated emulsion microcrystals with the spectra of crushed and large melt-grown AgCl single crystals, it has been shown that this sec-
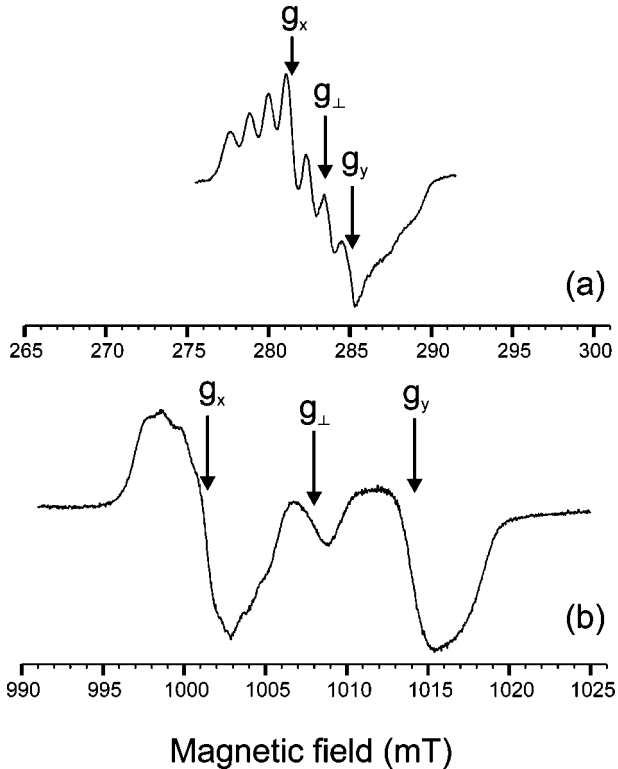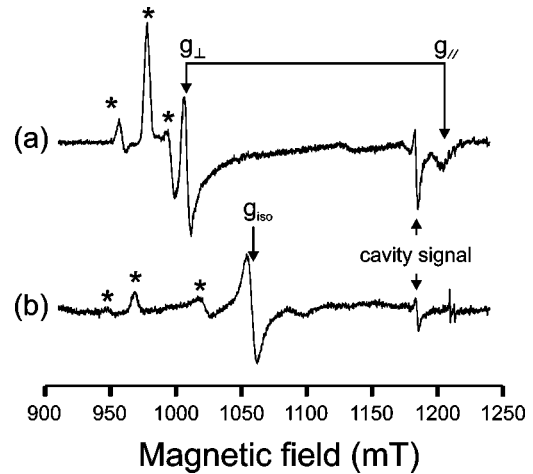

FIG. 3. EPR spectrum of AgCl microcrystals doped with approximately 100 ppm Rh^{3+} after x-ray irradiation at room temperature, recorded at (a) 20 K and (b) room temperature. The principal g components of the nonlocally charge-compensated $[RhCl_6]^{4-}$ complex are indicated ($g_{\parallel}$, $g_{\perp}$, g_{iso}). Spectral components of hydrated Rh^{2+} complexes are marked with an asterisk.

FIG. 2. Low-field part of (a) the X-band (9.56 GHz) and (b) the Q-band (34.0 GHz) EPR spectra of melt-grown, Rh^{2+} doped AgCl single crystals, recorded at 20 K with the magnetic field along a $\langle 100 \rangle$ direction.
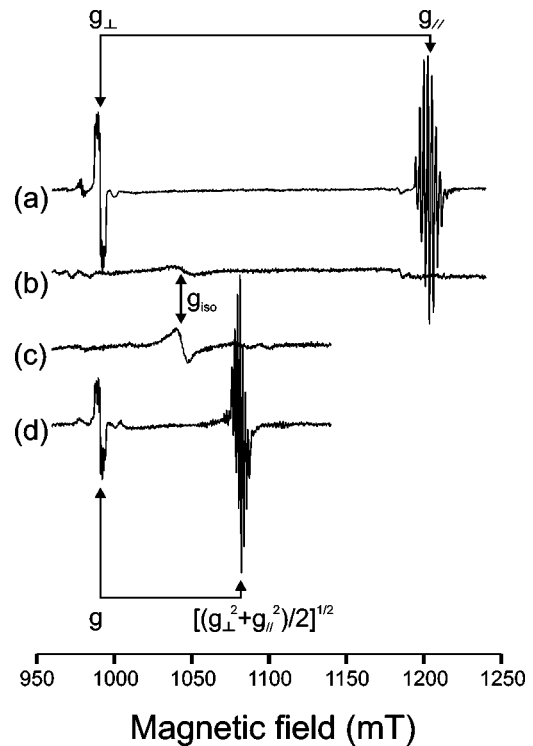

FIG. 4. EPR spectra of solution-grown NaCl single crystals doped with approximately 200 ppm Rh^{3+}, after x-ray irradiation at room temperature recorded (a) at 30 K with $B\|\langle 100 \rangle$, (b) at room temperature with $B\|\langle 100 \rangle$, (c) at room temperature with $B\|\langle 110 \rangle$, and (d) at 30 K with $B\|\langle 110 \rangle$. The g components of the nonlocally charge-compensated $[RhCl_6]^{4-}$ complex are indicated. The weaker EPR signals in the spectra are due to complexes compensated by one and two cation vacancies and to hydrated complexes (B center) (Ref. 8).

ond complex is also present in AgCl single crystals, be it in a lower concentration than the dominant complex with one next-nearest-neighbor cation vacancy. Figure 2 presents a detail of the $g_x - g_y$ region of the low-temperature EPR spectrum (20 K) of a Rh^{2+}-doped AgCl single crystal, recorded with the magnetic field along a $\langle 100 \rangle$ direction, at X- and Q-band microwave frequencies. Although the X-band spectrum might be interpreted as due to a single Rh^{2+} center, the presence of a second center becomes clear in the Q-band spectrum. No deviations from axial g tensor symmetry could be detected for the latter complex. This strongly indicates that the center is nonlocally charge compensated and that its symmetry observed at low temperature is due to a static Jahn-Teller elongation. Thus, it is analogous to the dominant Rh^{2+} complex in solution-grown NaCl single crystals.[8]

Comparison of the $[RhCl_6]^{4-}$ EPR spectra in AgCl emulsion microcrystals at low and room temperature gives further support to this assignment (see Fig. 3). The low-temperature spectrum shows, apart from the spectra of hydrated Rh^{2+} complexes, an intense signal of the axial $[RhCl_6]^{4-}$ complex, but no signal of the orthorhombic, charge-compensated complex. At room temperature the most intense signal is due to a cubic center with $g_{iso} \approx (g_\parallel + 2g_\perp)/3$, resulting from the thermal hopping of the Jahn-Teller elongation axis between the three equivalent $\langle 100 \rangle$ directions of the complex. The equivalence of the three $\langle 100 \rangle$ directions indicates that no charge compensating vacancies are near the complex. A temperature behavior similar to this is observed for the nonlocally charge-compensated $[RhCl_6]^{4-}$ complex in solution-grown NaCl single crystals (see Fig. 4) and has previously also been reported for the Ni^+ complex in AgCl in the absence of cation vacancies.[6]

The presence of this second, nonlocally compensated Rh^{2+} complex in AgCl single crystals now allows a simple and satisfactory explanation of the temperature dependence of the EPR spectrum. As the temperature is raised, the observed EPR spectrum of the complex compensated by one cation vacancy changes from orthorhombic to tetragonal symmetry, whereas that of the nonlocally charge-compensated complex changes from tetragonal to cubic. Both changes are a result of a static Jahn-Teller effect and are thus completely reversible with temperature. The disappearance of the high-temperature spectrum with tetragonal symmetry of the charge compensated Rh^{2+} complex at temperatures above the ambient may simply be a result of the relaxation properties of these complexes. In NaCl, the spectrum of the similar complex is reported to disappear at $T = 525$ K.[5] The difference in relaxation properties between the two Rh^{2+} complexes in AgCl, as a result of which the isotropic Rh^{2+} center remains detectable at 400 K, is most probably caused by the presence or absence of the next-nearest-neighbor cation vacancy.

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