

Reanalysis and identification of an Rh^{2+} dimer center in NaCl by combined application of 9.5 and 95 GHz EPR†

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A combined 9.5 (X-band) and 95 GHz (W-band) EPR study of an Rh^{2+} dimer center in Bridgman-grown rhodium-doped NaCl is presented. A close-to-tetragonal symmetry, similar to that of the monomer centers, with dominant symmetry axis along $\langle 001 \rangle$, the z -axis, is observed for this defect. The dimer and monomer spectra, which strongly overlap in the X-band spectra, could be well separated in the W-band measurements due to the higher g -resolution at higher magnetic fields. The anisotropy in the perpendicular plane, with $\langle 110 \rangle$ symmetry directions, is shown, from the combined X- and W-band spectra, to derive predominantly from a field-independent contribution, *i.e.* an orthorhombic spin–spin interaction, $\mathbf{S}_1 \cdot \mathbf{D} \cdot \mathbf{S}_2$ ($S_1 = S_2 = 1/2$), while the g matrices are near to axial, as in the case of the $\text{RhCl}_6^{4-} \cdot 2\text{Vac}$ monomer center (Vac = cation vacancy). This dimer center is shown to consist of a square arrangement of two substitutional Rh^{2+} ions and two next-nearest neighbor cation vacancies in an $\{001\}$ -plane, with the Rh^{2+} ions on opposite corners at a distance of *ca.* 7.6 Å, as estimated from the magnitude of the dipolar interaction. This work illustrates the ability of combined EPR experiments at widely different frequencies to discriminate field-independent from field-dependent terms in the spin-Hamiltonian.

I Introduction

Recently, detailed investigations by X-band EPR,^{1,2} electron–nuclear double resonance^{1,3,4} (ENDOR) and magnetic circular dichroism⁵ (MCD) have been reported on monomeric Rh^{2+} -defects in NaCl single crystals. In each of these centers, the Rh^{2+} ($3d^7$) ion is in a cation site, with a d_{z^2} orbital forming a preferential molecular bond with two Cl^- -ions in a $\langle 100 \rangle$ crystal direction, which we will label the z -direction from now on. The three dominant defects are called the O(I), O(II) and RTAX centers, or alternatively $\text{Rh}^{2+} \cdot n\text{Vac}$ with $n = 2, 1$ and 0, corresponding to two, one, or no cation vacancies in next-nearest neighbor (nnn) positions with respect to Rh^{2+} in the equatorial plane (I and II indicate symmetry and do not relate to the number of vacancies). This yields two near-to-tetragonal defects with a small orthorhombic distortion in the equatorial plane for O(I) and O(II) along the $\langle 110 \rangle$ - and $\langle 100 \rangle$ -directions, respectively. An axial EPR spectrum is found for the RTAX center, which has no associated vacancies. The defects are produced by various thermal and irradiation treatments, with important differences between crystals grown from the melt (Bridgman method), or from aqueous solution. These investigations are directly related to the study of rhodium impurities in AgCl microcrystals,⁶ where these ions act as deep electron traps and influence the photographic process.

In Bridgman-grown crystals, a related near-to-axial spectrum was also reported,¹ strongly overlapping with the monomer spectra observed in X-band EPR. From the limited data available it was ascribed to a Rh^{2+} dimer center, with

orthorhombic g matrix and magnetic dipolar interaction between the unpaired spins. We report here combined EPR measurements at 9.5 (X-band) and 95 GHz (W-band) from which an accurate determination of the spin-Hamiltonian of this defect is performed, permitting a clear distinction between the effects of field-dependent (Zeeman) and field-independent (spin–spin) contributions. On this basis, a microscopic defect model could be proposed.

II Experimental

The X-band and W-band measurements, at microwave frequencies close to 9.5 and 95 GHz, were performed in continuous wave EPR-spectrometers, BRUKER ESP300E and BRUKER ElexSys E600, respectively. In both cases, the measurements were performed at $T = 50$ K using appropriate helium cryostats (Oxford Instruments). The NaCl crystals were grown by the Bridgman method under a Cl_2 atmosphere with 0.8 wt. % $\text{Na}_3\text{RhCl}_6 \cdot 12\text{H}_2\text{O}$ added in the melt. The experiments were performed on as-grown crystals stored for long periods at room temperature. Fast annealing from higher temperatures, which one expects to disperse aggregates of Rh^{2+} -cation vacancy complexes, yields indeed a decrease in the intensity for the dimer spectra reported below. Crystals were cleaved from the rods with typical dimensions $3 \times 3 \times 5$ mm³ and $0.4 \times 0.4 \times 2$ mm³ for the X-band and W-band experiments, respectively.

III Experimental results and analysis

In Fig. 1 and 2 the X-band EPR spectra of the Rh^{2+} defects in NaCl are shown for a series of orientations of the magnetic field in a $\{100\}$ -plane. The spectra are dominated by the O(II) center which possesses a near-to-axial g matrix (with small orthorhombicity along $\langle 100 \rangle$ symmetry-axes, see Table 1). For certain orientations a distinct seven-line superhyperfine

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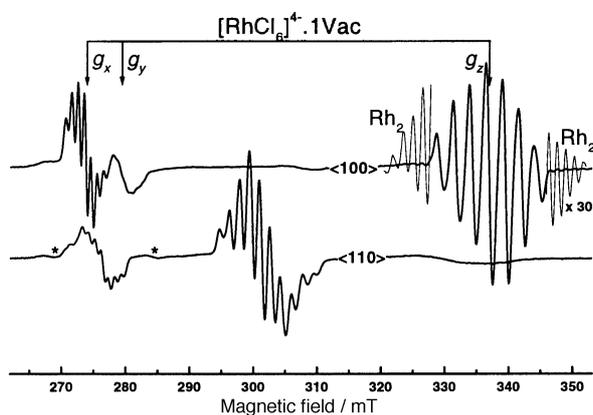


Fig. 1 X-band ($\nu = 9.44$ GHz) EPR spectra, taken at 50 K, of the as-grown rhodium-doped NaCl crystal. The two spectra were measured with the magnetic field parallel to a $\langle 100 \rangle$ and a $\langle 110 \rangle$ orientation. The asterisk indicates transitions of the dimer species. Only around the high-field septet along $\langle 100 \rangle$ of the $\text{Rh}^{2+} \cdot 1\text{Vac}$ center, are resonances of the dimer center clearly observed. These lines are magnified ($\times 30$) in the figure.

(shf) pattern is observed, arising from interaction with two equivalent Cl^- ions along the principal symmetry axis, the z -axis. On both sides of the parallel spectrum for $H \parallel \langle 100 \rangle$, and on both sides of the perpendicular spectrum for H close to $\langle 110 \rangle$, additional lines are observed which can be followed over only a limited part of the angular variation (Fig. 2). In the case of the parallel spectrum, these lines can be viewed as the outer part of an shf-pattern. However, their study is hampered by the low intensity and the overlap with the O(II) spectrum. These lines were attributed by Schweizer and Spaeth¹ to an Rh^{2+} dimer center with orthorhombic g matrix (g_x, g_y, g_z along, e.g. $[110], [1\bar{1}0]$ and $[001]$, respectively). In this model one would predict, for each field orientation, a pair of transitions resulting from the magnetic dipole interaction between the two $S = 1/2$ spins.

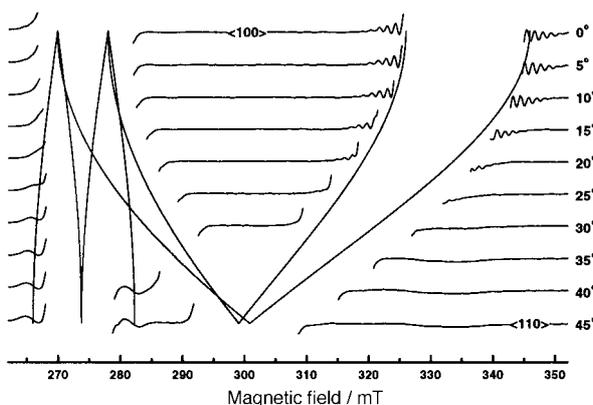


Fig. 2 X-band ($\nu = 9.44$ GHz) angular variation at 50 K in a $\{100\}$ plane. The lines of the $\text{Rh}^{2+} \cdot 1\text{Vac}$ center are omitted to simplify the spectrum. The solid “vertical” curves show the calculated¹⁰ angular variation of the line center positions using the D and g values from Table 1.

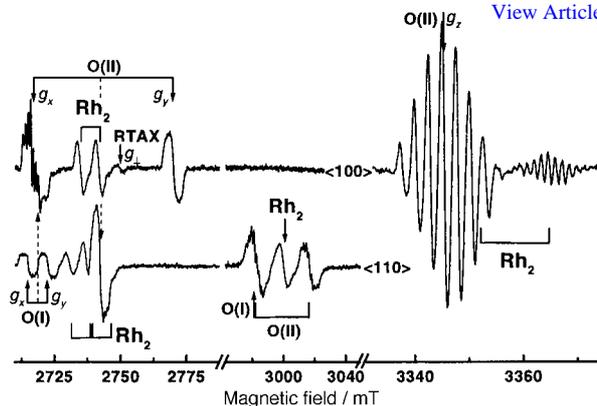


Fig. 3 W-band ($\nu = 94.2915$ GHz) EPR spectra at 50 K with the magnetic field parallel to a $\langle 100 \rangle$ and a $\langle 110 \rangle$ orientation. The different Rh^{2+} centers present in the as-grown NaCl crystal are indicated. The spin-Hamiltonian parameters of these centers can be found in Table 1. Note the different magnetic field scales in the different parts of the spectrum.

In the corresponding high-frequency spectra measured in the W-band (see Fig. 3) the different Rh^{2+} spectra are clearly separated, due to the higher g -resolution. In particular, dimer lines are now clearly observed in each of the main field orientations. The relative intensities have changed in favor of the dimer spectrum, which is up to now an unexplained effect. In the g_{\perp} region of the $\langle 100 \rangle$ spectrum, the dimer pair is very clearly observed (see Fig. 3 and 4). Also in the parallel spectrum, a line with resolved shf structure is found at the high-field side of the O(II) spectrum; it turns out that this is the high-field component of the pair, of which the low-field component is hidden under the O(II) spectrum. The observed seven-line shf structure points again to interaction with two equivalent Cl^- nuclei, but the splittings amount to about half

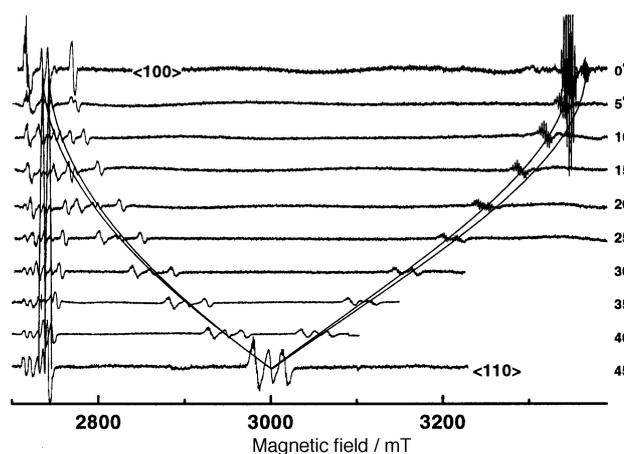


Fig. 4 W-band ($\nu = 94.2915$ GHz) angular variation at 50 K in a $\{100\}$ plane. The angular variation of the line center positions was calculated¹⁰ using D and g values from Table 1.

Table 1 Spin-Hamilton parameters of various Rh^{2+} centers, monomeric or dimeric, in sodium chloride single crystals

center	g_x	g_y	g_z	$A_x(^{35}\text{Cl})$	$A_y(^{35}\text{Cl})$	$A_z(^{35}\text{Cl})$	ref.
$\text{Rh}^{2+} \cdot 2\text{Vac}$ O(I) ^a	2.4797 ₄	2.4712 ₄	2.0118 ₈	33.9 ± 0.1	33.9 ± 0.1	72.7 ± 0.2	2, 4
$\text{Rh}^{2+} \cdot 1\text{Vac}$ O(II) ^b	2.4779 ₄	2.4301 ₄	2.0154 ₈	35 ± 1	35 ± 1	73 ± 2	2
$\text{Rh}^{2+} \cdot 0\text{Vac}$ RTAX ^c		2.4510 ₁	2.0190 ₁	33.9 ± 0.1		75.5 ± 0.2	3
$\text{Rh}^{2+} - \text{Rh}^{2+} \cdot 2\text{Vac}$	2.4609 ₄	2.4599 ₄	2.008 ₁	Est. at 34		72.4	This work
	$D_x = 0 \pm 20,$		$D_y = +340 \pm 20,$		$D_z = -340 \pm 20$		

The chlorine superhyperfine and the fine-structure parameters are expressed in MHz. ^a Principal directions of g and A matrices are along, e.g. $x \parallel [110], y \parallel [1\bar{1}0],$ and $z \parallel [001]$. ^b Three principal directions along $\langle 100 \rangle$ directions. ^c Axial with $z \parallel \langle 100 \rangle$.

of that of the corresponding O(II) line. The dimer transitions can be followed from the parallel to the perpendicular orientation between the two lines of the O(II) center.

In Fig. 5 an expanded view is shown of the angular variation of the spectrum in the g_{\perp} region, in which the dimer spectrum can be followed for all angles, although it still partially overlaps with the O(II) spectrum for $H \parallel \langle 110 \rangle$. In this orientation one also finds lines of the O(I) spectrum well separated from the other spectra,² which demonstrates the presence of the O(I) monomer center in the Bridgman crystals without further treatment. As already indicated by the X-band spectra, the dimer lines in the g_{\perp} region are moving to extrema for $H \parallel \langle 110 \rangle$, pointing to orthorhombic symmetry along such axes. However, from g anisotropy a tenfold increase in the angular variation in line position would have been expected for W-band compared to X-band measurements. For instance, the g factors derived in ref. 1 ($g_x = 2.480$, $g_y = 2.420$) would, at 95 GHz, have led to a splitting of *ca.* 70 mT between the corresponding lines, in conflict with our experimental results. The W-band measurements demonstrate that the x - y anisotropy is not dominated by the field-dependent Zeeman interaction, but by field-independent spin-spin interactions.

The Rh^{2+} dimer spectra have been analyzed using the spin-Hamiltonian

$$\mathcal{H} = H \cdot g \cdot (S_1 + S_2) + S_1 \cdot D \cdot S_2 + g_0 \mu_B \sum_{i=1,2} S_i \cdot A \cdot (I_{ix} + I_{iy}) \quad (1)$$

with the electron spins of two equivalent rhodium ions $S_i = 1/2$ ($i = 1, 2$), the nuclear spins of four chlorine ions $I_{ix} = I_{iy} = 3/2$, and the matrices g and A and the tensor D , of the Zeeman, shf, and fine-structure interactions, respectively. All three matrices possess principal directions along, *e.g.* $x \parallel [110]$, $y \parallel [1\bar{1}0]$ and $z \parallel [001]$. The choice of the z -axis is in line with that for the monomer centers, corresponding to the near-to-axial direction defined by the d_{z^2} ground-state orbital. The fine structure is a small perturbation on the Zeeman interaction and the shf interaction is again much smaller, as derived from the observed line splittings. In a first-order approximation, it can be shown that only the traceless part of the D tensor determines the EPR transitions⁷ and, therefore, only this part has been considered in the analysis.

The fine-structure interaction then yields a doublet for each field orientation⁷ which, for each of the three principal directions, is split by $\Delta_i = \frac{3}{2}(h|D_i|/g_i\mu_B)$ ($i = x, y, z$), with D_i the principal value of the traceless part of the D tensor. The parameters for best fitting of the X- and W-band spectra are listed in Table 1 and compared to those of several monomer

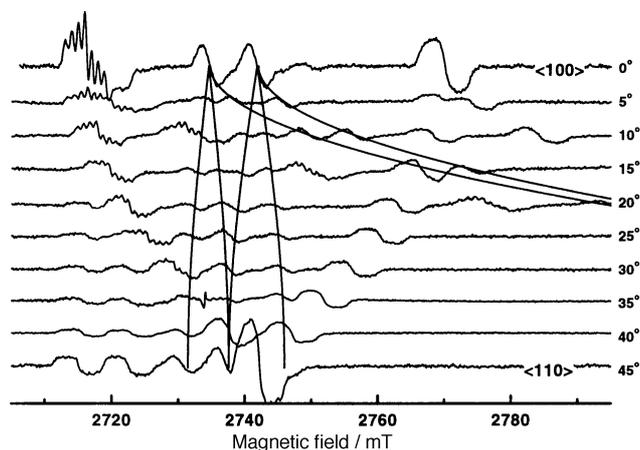


Fig. 5 Detail of the W-band ($\nu = 94.2915$ GHz) angular variation of Fig. 4 in the g_{\perp} region. The angular variation of the line center positions was calculated¹⁰ using D and g values from Table 1.

Rh^{2+} defects in NaCl. A combined fitting at both frequencies is only possible for a g matrix with near-to-axial symmetry, $g_x \approx g_y$. The resulting angular variation of the allowed transitions is shown in Fig. 2, 4 and 5, for both microwave frequencies. The collapse of the doublet in a singlet in the angular variation from the parallel to the perpendicular direction, around 45° , results from the opposite signs of D_y and D_z . The splitting also vanishes for the x -direction because $D_x \approx 0$. The strong similarity of the g matrix of this defect with that of the monomer centers shows that the Rh^{2+} dimer center consists essentially of a pair of weakly interacting Rh^{2+} ions in the same electronic state as in the case of the monomer defects.

It is possible to estimate the very small orthorhombicity of the g matrix by a careful fitting of the low-field lines along the $\langle 110 \rangle$ orientation. This yields a very small, but non-zero, anisotropy $g_x - g_y = 0.00106$, nearly an order of magnitude less than the O(I) center, the monomer center with the same symmetry (see Table 1).

In the parallel direction ($H \parallel z$) a well-resolved seven-line chlorine shf structure is observed in the W-band measurement, as for the O(II) monomer spectrum. However, the line separation is only half that of the monomer case, leading, in the weakly interacting dimer model,⁷ to a similar value of A_{\parallel} (see Table 1). From this value, and from the position of the outer shf lines of the dimer doublet on both sides of the O(II) X-band spectrum for $H \parallel z$, the doublet splitting and, hence, the D_z value could be determined, as well as an accurate g_z value. For the other field directions away from the defect's z -axis, the shf-structure becomes unresolved, as was also observed for some of the monomer lines. However, an estimate of the shf splittings could be obtained from the shape of the dimer lines in the perpendicular spectrum, and could be compared to those of the O(I) and O(II) spectrum at 95 GHz. This again yields half the splitting for the dimer than for the monomer spectra. These observations fully agree with the assumptions contained in the dimer spin-Hamiltonian (1), which yields half the line splitting for values of the shf parameters comparable to those of the monomer centers (see Table 1).

IV Discussion

The dominant monomeric Rh^{2+} center in the as-grown NaCl crystal is an Rh^{2+} ion on a cation site with one associated cation vacancy, *i.e.* the O(II) center.¹ The Rh^{2+} vacancy pairs form electrical dipoles that can, *e.g.* during slow cool-down after Bridgman-growth, agglomerate and form an appreciable amount of dimers if the impurity concentration is sufficiently high. Anti-parallel alignment of the two dipoles is expected to yield the most stable configurations. In Fig. 6 a dimer configuration in a $\{100\}$ plane is depicted, which is obtained by a simple arrangement of two O(II) centers, and which possesses the orthorhombic symmetry observed in the angular variation

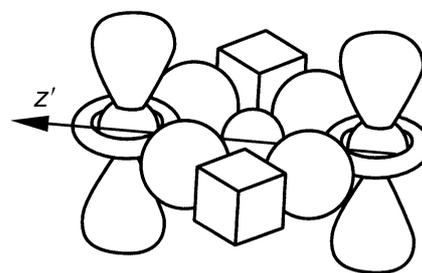


Fig. 6 Model for the Rh^{2+} dimer in NaCl: a square arrangement in a $\{100\}$ plane of two Rh^{2+} ions of opposite corners with two next-nearest neighbor vacancies in the other corners. The dipolar $y = z'$ axis is the axis connecting the Rh^{2+} ions. The size of the d_{z^2} orbitals is exaggerated in the z direction.

of the spectra. This model will be shown to be consistent with our experimental findings, while other possible pair geometries have to be discarded.

In this model, the axis that connects both Rh^{2+} ions is oriented along a $\langle 110 \rangle$ direction, which defines the main axis $z' \parallel y$ of the magnetic dipole interaction between the paramagnetic ions. In this case, the interionic axis does not coincide with the symmetry axis of the near-to-axial \mathbf{g} matrix. Noting that the two axes $x \parallel \langle 110 \rangle$ and $z \parallel \langle 100 \rangle$ perpendicular to the dipolar axis are strongly inequivalent, due to the d_{z^2} ground orbital with the molecular bond and the resulting axial \mathbf{g} matrix along the z -axis, it is not surprising that the experimental (traceless) \mathbf{D} tensor is orthorhombic. In the conventional reference frame of the dipolar interaction ($x' \parallel z, y' \parallel x, z' \parallel y$), one can rewrite the fine-structure term of the spin-Hamiltonian in terms of the usual D and E parameters,^{7,8}

$$\begin{aligned} \mathcal{H}_{\text{fs}} &= \mathbf{S}_1 \cdot \mathbf{D} \cdot \mathbf{S}_2 \\ &= D(3S_{1z'}S_{2z'} - \mathbf{S}_1 \cdot \mathbf{S}_2) + E(S_{1x'}S_{2x'} - S_{1y'}S_{2y'}) \quad (2) \end{aligned}$$

This corresponds to a \mathbf{D} -tensor

$$\begin{aligned} \mathbf{D} &= \begin{bmatrix} D_x = D_{y'} & 0 & 0 \\ 0 & D_y = D_{z'} & 0 \\ 0 & 0 & D_z = D_{x'} \end{bmatrix} \\ &= \begin{bmatrix} -D - E & 0 & 0 \\ 0 & +2D & 0 \\ 0 & 0 & -D + E \end{bmatrix} \quad (3) \end{aligned}$$

The resulting values for this choice of reference frame are $D = -170 \pm 10$ MHz and $E/D = -1.0 \pm 0.1$. A sign of uncertainty remains in the experimental determination of principal values of \mathbf{D} and, therefore, also in D and E . The chosen negative sign for D corresponds to the expected sign for pure magnetic dipole interactions (see below).

The classical interaction between magnetic point dipoles, taking into account g anisotropy (axial approximation, $g_x = g_y = g_{\perp}$ and $g_z = g_{\parallel}$), yields a relationship between D and the distance r between the two dipoles:[§]

$$D = -\frac{1}{6} (5g_{\perp}^2 + g_{\parallel}^2) \frac{\mu_B^2}{r^3} \quad (4)$$

From $D \approx -170$ MHz (and $\mu_B^2/h = 12980 \text{ \AA}^3$ MHz), one finds $r = 7.6 \text{ \AA}$. This figure should be compared with 7.98 \AA , the distance between the Rh^{2+} sites in our model, *i.e.* twice the NaCl interionic distance along $\langle 110 \rangle$, which was taken from ref. 9. These numbers are very close to each other, taking into account the rough dipole-dipole approximation, and the possibility of lattice relaxation in the defect. This lends further support to the proposed model.

It does not seem meaningful to compare the interionic distance estimated by Schweizer and Spaeth,¹ on the basis of the limited X-band data, with our present result. Indeed, their analysis was based on an orthorhombic \mathbf{g} matrix combined with a pure dipolar interaction between the Rh^{2+} ions, with an interionic axis along $\langle 100 \rangle$, as can be deduced from the reported angular variation. This is in conflict with our W-band data. Also, a different expression is used for the magnitude of the dipolar interaction. Finally, their estimate of $r \approx 5.5 \text{ \AA}$ is very small and would only stem from an intercationic distance along $\langle 100 \rangle$. Such a dimer configuration has to be eliminated, as will be discussed below.

Expression (4) relates the spin-Hamiltonian parameters D to the microscopic distance r between the two unpaired spins. Due to the g anisotropy in the x - z plane, perpendicular to the

interionic axis, a non-zero E parameter results from the point-dipole formalism:⁷ $E = 1/2(g_{\perp}^2 - g_{\parallel}^2)\mu_B^2/r^3$. Theoretically, filling the experimental g values, one would expect for E/D :

$$\left(\frac{E}{D}\right)_{\text{theoretical}} = -\frac{3(g_{\perp}^2 - g_{\parallel}^2)}{5g_{\perp}^2 + g_{\parallel}^2} \approx -0.15. \quad (5)$$

The experimentally determined value of this ratio $E/D = -1.0 \pm 0.1$ is nearly an order of magnitude higher. However, only pure point-dipole interactions were considered, and it seems that a more subtle treatment is required. First, one has to consider the anisotropic distribution of the electrons, not only in the Rh^{2+} orbitals, but also on the two adjacent Cl^- ions which were shown to each carry up to 12% of the spin density in the monomer defects.⁴ The largest electron density is along the molecular z axes, *i.e.* orthogonal to the dipolar z' axis, along which also the dominant molecular binding also takes place with the two chlorines. As mentioned above, the principal axes of the \mathbf{D} tensor point to inequivalent crystal directions, a feature not accounted for in the point-dipole model. Finally, exchange, *i.e.* superexchange *via* the neighboring ions or pseudo-dipolar exchange,^{8,11} is likely to occur and may contribute a small anisotropic interaction causing apparent changes in the dipolar interaction. However, the contribution of pseudo-dipolar exchange⁸ is expected to be small, since no orbital degeneracy is left in the ground state, which is a consequence of molecular binding or, in an alternative picture, the result of a static Jahn-Teller effect.² In such a case, the pseudo-dipolar exchange is a third-order effect $\propto (\Delta g)^2 J$, where $\Delta g = 2.0023 - g_{\perp}$ and J is the exchange interaction between the ground state of one ion and one of the low-lying excited states of the other ion in the dimer. These interactions are expected to be very small considering that the ions are 7.6 \AA apart, and also that the ground-state d_{z^2} orbitals are pointing perpendicular to the Rh^{2+} - Rh^{2+} axis. Unfortunately, neither the half-field, nor the singlet-triplet transitions could be experimentally detected in the present dimer spectrum, and thus the exchange parameter in the spin Hamiltonian was not determined.

The \mathbf{g} matrix of the Rh^{2+} ions in the dimer is very close to axial, which is somewhat puzzling. In ref. 4 it was already discussed that, in a point-ion approximation the \mathbf{g} matrix of the $\text{O(I)} = \text{Rh}^{2+} \cdot 2\text{Vac}$ center should be axial, if no relaxation from the lattice positions is considered. Here, only admixture of states within the d^7 configuration was taken into account. The orthorhombic component, therefore, results from either lattice relaxation, or admixture of other configurations by the odd crystal-field components. If the Rh^{2+} ion in the $\text{O(I)} = \text{Rh}^{2+} \cdot 2\text{Vac}$ center is compared to each of the ions in the dimer, the resemblance between the configurations is striking (see Fig. 6). In the dimer center, compared to O(I) , the crystal field at one of the Rh^{2+} sites differs only by the contribution of the excess positive charge of the partner ion, which is at a larger distance than the two vacancies carrying an effectively negative charge. In the same approximation as considered for the O(I) center, this would again yield an axial \mathbf{g} matrix. The even smaller orthorhombicity of the dimer center should, therefore, be ascribed to a smaller relaxation of the surroundings, or to the smaller first-order field acting on the Rh^{2+} site due to the opposite effective charges of the vacancies and the partner metal ion, or to an accidental near-cancellation of the different contributions.

Another model for the dimer, including the tetragonal symmetry is hard, if not impossible, to find. A configuration in which the pair of Rh^{2+} ions would lie along the $z \parallel [001]$ direction should be excluded since this would give rise to inequivalent (axial) Cl^- shf interactions. Also, in this case, the fine-structure parameters would yield an estimated inter-nuclear distance $r = 7.2 \text{ \AA}$, which does not correspond to, *e.g.* once or twice the intercationic distance along $\langle 001 \rangle$. This configuration would also imply a purely dipolar interaction

§ One can easily reproduce expressions (4) and (5) using the footnote on p. 445 in ref. 8, and setting $g_{x'} = g_{\perp}$, $g_{y'} = g_{\parallel}$, and $g_{z'} = g_{\perp}$.

($E = 0$) with $D_x = D_y$, which is in conflict with the observations. A second possible configuration of the dimer could be with the two Rh^{2+} ions along a $\langle 100 \rangle$ axis perpendicular to the preferential axis of the d_{z^2} orbital, but this again cannot be reconciled with the experimental observation of two symmetry axes along $\langle 110 \rangle$ directions. Finally, a tempting model consists of the Rh^{2+} ions arranged as in Fig. 6, but without the cation vacancies. However, uncompensated Rh^{2+} ions are present only at very low concentration in this crystal (see the weak RTAX line in Fig. 3) and, moreover, the Coulomb repulsion between the two excess positive charges would act strongly against dimer formation. The above models must be rejected and a square arrangement in a $\{001\}$ plane of the two Rh^{2+} ions in opposite corners with two next-nearest neighbor vacancies in the other corners is considered as the most likely configuration (see Fig. 6).

V Conclusions

The dominant Rh^{2+} center in Bridgman-grown NaCl crystals is an Rh^{2+} vacancy pair, the O(II) or $\text{Rh}^{2+} \cdot 1\text{Vac}$ center. These pairs are found to agglomerate and form pairs of Rh^{2+} vacancy dipoles, the observed Rh^{2+} dimer centers. The ground electronic state of the individual Rh^{2+} ions in the dimer strongly resembles that in the O(I) or $\text{Rh}^{2+} \cdot 2\text{Vac}$ centers, also present in these crystals. The two $S = 1/2$ paramagnetic ions in the dimer center are coupled by the magnetic dipolar, and probably also by weak spin exchange interactions. From the magnitude of the dipolar interaction, a distance of 7.6 Å was determined between the two Rh^{2+} ions.

From a combined X-band and W-band EPR investigation, it was possible to unravel the different field-dependent and field-independent interactions in the spin-Hamiltonian: the orthorhombicity in the x - y plane was shown to be dominated by the dipolar interaction and not by g anisotropy, as suggested earlier on the basis of X-band EPR only.¹ From these results it was possible to determine the structure of the dimer

center, which consist of a symmetrical square arrangement of two Rh^{2+} ions and two cation vacancies in a $\{100\}$ plane.

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