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Temperature variation of the ESR parameters of the self-trapped-electron center in $PbCl_2$

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The self-trapped-electron center in $PbCl_2$ crystals, i.e., the Pb_2^{3+} molecular ion resulting from the trapping of a conduction electron by a pair of Pb^{2+} lattice cations along the a direction, exhibits in the 10–78 K temperature range a strong temperature dependence in both g and hyperfine tensors of the ESR spectrum. Such an unusual large variation, which is not observed for the isoelectronic Tl_2^+ and Pb_2^{3+} impurity centers in alkali chlorides, seems to be related to the anisotropic thermal expansion of the layered $PbCl_2$ lattice.

It has been recently shown[1,2] that conduction electrons produced by illumination more energetic than the band gap in pure $PbCl_2$ crystals are trapped at cation sites, resulting in paramagnetic self-trapped-electron (STEL) centers. From the analysis of the associated electron spin resonance (ESR) spectrum, observed at low temperature (T = 13 K) after x-ray irradiation or uv illumination at 80 K, it has been inferred that the electron is trapped at a pair of nearest-neighbor Pb^{2+} cations along the a direction of the $PbCl_2$ lattice. The resulting STEL center represents a paramagnetic Pb_2^{3+} molecular ion with electron configuration complementary to that of the X_2^- (X= halogen) self-trapped-hole center in alkali halides.[3]

Selective optical bleaching experiments at low temperature suggest[2] that the STEL center represents the initial step in the photoinduced formation of lead clusters and in the photochemical decomposition of lead halides at temperatures where diffusion of anion vacancies occurs.[4] Moreover, these results suggest, in agreement with previous optical studies,[5,6] that the self-trapped exciton in $PbCl_2$ consists of a hole trapped in an excited orbital around the Pb_2^{3+} center. Such a molecular-type exciton localized at cation sites, in which the electron is the heavier component, requires further investigation from the point of view of both energy level structure and decay modes.

In view of the fundamental character of the STEL center we considered it worthwhile to study the temperature dependence of its ESR parameters in the broadest temperature range available for observation, i.e., from 10 K to 78 K. The results show an unusually strong temperature variation of both g and A tensor components, very different from the insignificant variation observed in the case of the isoelectronic Tl_2^+ and Pb_2^{3+} impurity centers in KCl and NaCl, respectively.[7–9] The observed strong temperature variation seems to be due to the anisotropic thermal expansion of the layered $PbCl_2$ lattice, resulting in a variation of both local crystal field components and molecular bond length of the STEL center.

The ESR measurements were performed on the same samples employed in a previous study,[1] prepared from oxygen-free $PbCl_2$ single crystals grown by the Bridgman technique. The STEL centers were produced by x-ray irradiating (W cathode, 50 kV, 50 mA) the samples at 80 K, followed by their transfer in the cold region (T = 10 K) of the microwave cavity, without any intermediate warmup. In view of the small penetration depth of the x rays in $PbCl_2$ the concentration of the STEL centers has been increased by irradiating the samples on each side. The larger amount of resulting STEL centers did allow the observation of the corresponding ESR spectra up to $T \approx 80$ K, although the intensity strongly decreased above 50 K due to relaxation-induced broadening effects. The x-ray irradiation, as well as the subsequent handling of the samples, were performed under ambient red light in order to avoid any optical bleaching effects.[2]

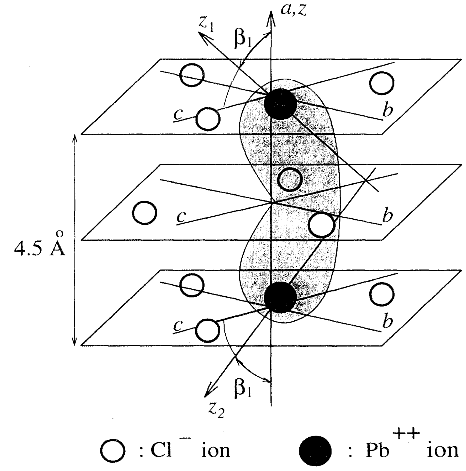

FIG. 1. The structure of the STEL center in $PbCl_2$, as inferred from the analysis of the ESR data. The bending of the unpaired electron cloud is reflected in the tilting of the hf tensor main axis z_1 with respect to the g tensor z axis. The Pb nuclei are represented in an inward displaced (relaxed) position with respect to their positions in the pure $PbCl_2$ lattice.

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TABLE I. The principal values of the g and hf tensors components A (in mT) of the bent molecular Pb_2^{3+} (STEL) center in $PbCl_2$ and of the isoelectronic linear Pb_2^{3+} impurity dimer centers in NaCl.

Center	T (K)	g_x	g_y	g_z	A_x	A_y	A_z
STEL in $PbCl_2$[a]	10	1.550	1.374	1.719	−82.8	−85.3	111.7
	78	1.492	1.322	1.663	−91	−92	111
Pb_2^{3+}(I) in NaCl[b]	15	1.438	1.222	1.625	−122	−117	125
Pb_2^{3+}(III) in NaCl[b]	15	1.469	1.300	1.621	−123	−115	115

[a] Estimated experimental errors in g_i and A_i are smaller than ±0.001 and 1 mT, respectively. The orientation of the g and A tensors main axes are given in the text and in Fig. 1.

[b] Experimental data from Ref. 8.

The ESR measurements were carried out on an X-band spectrometer, a Bruker model ESP-300E, equipped with a gas-flow cryogenic system operating in the 10–300 K temperature range.

As previously mentioned,[1] the ESR spectrum of the STEL center is fully described by the spin Hamiltonian consisting of the Zeeman term and the hyperfine (hf) interactions with the two neighboring Pb nuclei; thus,

$$\frac{1}{g_0\mu_B}\mathcal{H} = \frac{1}{g_0}\boldsymbol{H}\cdot\boldsymbol{g}\cdot\boldsymbol{S} + \boldsymbol{S}\cdot\boldsymbol{A}_1\cdot\boldsymbol{I}_1 + \boldsymbol{S}\cdot\boldsymbol{A}_2\cdot\boldsymbol{I}_2 \qquad (1)$$

in which $S = 1/2$. The hf tensors $\boldsymbol{A}_1$ and $\boldsymbol{A}_2$ have the same principal components and their axes are related by mirror symmetry with respect to the bc plane, perpendicular to the intramolecular axis (Fig. 1). The second and third terms occur only if the corresponding nucleus is the ^{207}Pb isotope (22% natural abundance) with nuclear spin $I = 1/2$. The other stable Pb isotopes are even (78% natural abundance) and have nuclear spin $I = 0$.

The g tensor components, as determined from the ESR transitions of the $^{\text{even}}Pb_2^{3+}$ isotopic species (Table I), have their principal z axis parallel to the a crystal axis and their x, y axes rotated by the angle $\gamma = \pm 10^0$ from the c and b crystal axes, respectively. They exhibit a strong temperature dependence (Fig. 2) without any measurable change in the orientation of their main axes. The linear dependence of all three g components results in the same variation of $\simeq -0.05$ in the 10 K to 78 K temperature range.

The A tensor components, determined by a computer diagonalization and fitting procedure involving the ESR transitions of the $(^{\text{even}}\text{Pb}-^{207}\text{Pb})^{3+}$ isotopic species (Table I), exhibit a quite similar behavior (Fig. 3). The A_x and A_y hf tensor components decrease linearly with increase in temperature, the maximum variations amounting to $\simeq -9$ mT and $\simeq -7$ mT, respectively. Meanwhile, the A_z hf tensor component remains practically constant in the same temperature range, within experimental errors (±0.7 mT). The x_1, y_1, z_1 main axes of the A hf tensor are rotated with respect to the c and b crystal axes

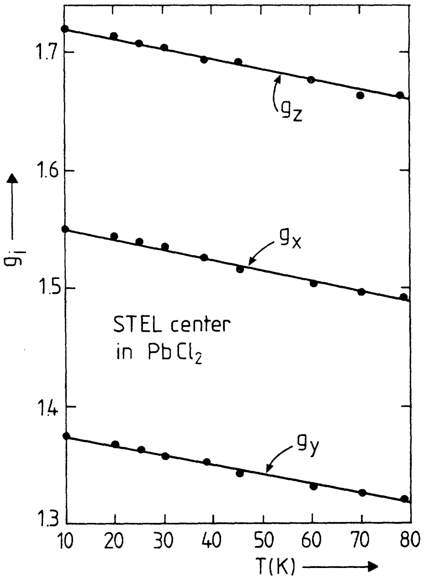

FIG. 2. Magnitude of the g tensor components for the Pb_2^{3+} (STEL) center in $PbCl_2$ crystals, plotted as a function of the measuring temperature. Interpolated (solid lines) and experimental (dots) variation are presented.

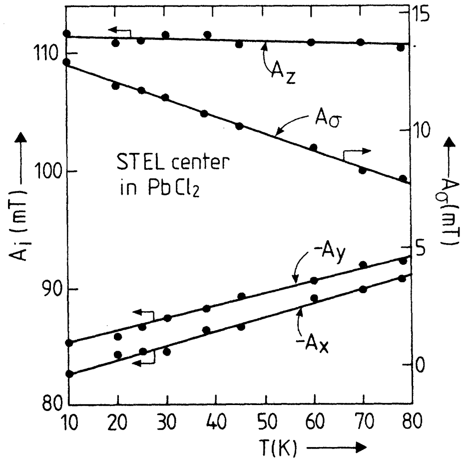

FIG. 3. Magnitude of the principal hf tensor components A_i and of the isotropic contribution A_σ to the hf interaction for the Pb_2^{3+} (STEL) center in $PbCl_2$, plotted as a function of the measuring temperature.

by the Euler angles $\alpha_1 = 0$ and $\beta_1 = \pm 33^0$. The third Euler rotation angle γ_1 is experimentally undetermined due to the quasiaxial character of the A hf tensor. As in the case of the g tensor, the orientation of the A hf tensor main axes does not change in the measured temperature range.

It should be mentioned that a paramagnetic defect attributed to a Pb_2^{3+} center has been recently reported in PbCl_2 single crystals which have been γ-ray irradiated and measured at liquid nitrogen temperature.[10] Although the hf tensor values were not reported in that paper, it seems, in comparison with the present results, that the same paramagnetic defect has been produced in both cases. This is supported by the similar values of the g tensor components and directions of its main axes measured at liquid nitrogen temperature. As expected, due to the higher penetration, the γ-ray irradiation resulted in larger defect concentrations. It would be interesting to see whether it is the higher defect concentrations, or the presence of added impurities (Cr,Ti,Ni) that causes the higher optical stability of the STEL centers produced by γ-ray irradiation, as seems to be the case.[10]

The present ESR measurements demonstrate, based on comparison with the isoelectronic $\mathrm{Tl}_2^+\langle 111\rangle$ center in KCl (Ref. 7) and Pb_2^{3+} center in NaCl (Ref. 8), that the g and hf tensor components of the STEL center in PbCl_2 exhibit a strong temperature dependence in the low temperature range (10–78 K). In the former case, variations of $0.002 < \Delta g_i < 0.005$ and $0.2 < A_i < 0.6$ mT have been reported[7] in the 13–65 K temperature range, one order of magnitude smaller than for the STEL center in PbCl_2 and close to the limit of experimental error. In recently performed ESR measurements we have found that the g and A tensor components of the Pb_2^{3+} centers in NaCl exhibit in the same temperature range only very small variations, close to the experimental accuracy.

The analysis of the spin Hamiltonian parameters of the earlier observed isoelectronic Tl_2^+ impurity dimer centers in alkali chlorides[7,9] and Pb_2^{3+} impurity dimer centers in NaCl (Ref. 8) has been performed by using the molecular model previously employed to explain the ESR properties of the V_k center in alkali halides.[3] The latter molecular defect possesses a complementary electron configuration. The model is consistent with the $D_{\infty h}$ symmetry of a free, linear diatomic molecular center subjected to the local crystal field with D_{2h} symmetry of the alkali chloride lattices.

In this model the paramagnetic electron is trapped by the two Pb^{2+} or Tl^+ ions into a σ_g molecular ground orbital, which is singly occupied and constructed mainly from the $6p_z$ orbitals of the two heavy metal ions, with admixture of $6s$ orbitals. The excited orbitals, π_g^x and π_g^y, at resulting energies E_{1g} and E_{2g} above the ground state, respectively, are mixed into σ_g by the spin-orbit interaction, contributing to both g and A hf parameters. It has then been possible to express, in a second-order perturbation calculation, the $\Delta g_i = g_0 - g_i$ shifts as a function of the λ_{gi}/E_g ratios and of some molecular parameters λ_i and δ_i, and the hf tensor components A_i as a function of the Δg_i shifts. It should be mentioned that the evaluation of the molecular parameters λ_i and δ_i, which are the matrix elements of the corresponding i components of the orbital part of the spin-orbit coupling between the ground state and the excited states and of the orbital angular momentum operator in the Zeeman operator, respectively, is far from trivial, requiring an accurate knowledge of the molecular σ_g and π_g wave functions, which depend on unknown variables such as the Pb-Pb internuclear distance, the magnitude of the crystal field, or the degree of electron delocalization on the neighboring lattice ions.

In the case of the STEL center in PbCl_2 the main axes of the hf tensors A_1 and A_2 are each tilted by an angle $\beta_1 = \pm 33^0$ with respect to the main z axis of the g tensor, which is parallel to the a crystal axis (Fig. 1). Due to the more localized character of the main hf compared to the electron Zeeman interaction, the orientation of the main axes of the hf tensors A_i reflects the local distribution of the unpaired electron cloud. Consequently, one concludes that the STEL center in PbCl_2 represents a diatomic molecular species with a bent molecular bond, exhibiting C_{2v} symmetry, with its C_2 rotation axis in the bc plane (Fig. 1). The bending of the STEL molecular center, as reflected in its symmetry change from $D_{\infty h}$ to C_{2v}, results in a new energy level structure in which the σ_g ground molecular orbital transforms into the $1a_1$ orbital and the excited molecular orbitals π_g^x and π_g^y transform into the $1a_2$ and $2b_2$ molecular orbitals.[11] Compared to the σ_g molecular ground orbital, the $1a_1$ molecular ground orbital also includes the $6p_y$ atomic orbitals. New atomic orbitals are also mixed into the excited $1a_2$ and $2b_2$ molecular orbitals. The spin-orbit interaction will now mix into the $1a_1$ ground state the a_2, b_1, and b_2 excited states, resulting in even more complicated expressions for both g and hf A tensor components with a larger number of atomic and molecular parameters, which are extremely difficult to estimate. Additional atomic orbitals have to be included in the expressions of the molecular orbitals of the STEL center if one considers the lower symmetry of the local crystal field as well. Indeed, the Pb_2^{3+} diatomic molecule in PbCl_2 is subjected to a low symmetry crystal field which has as symmetry element only the reflection in the bc plane. The resulting large number of additional, unknown parameters makes any quantitative analysis of the ESR data extremely difficult.

In our previous paper[1] we analyzed the ESR parameters of the STEL center, measured at low temperature, with the linear diatomic molecular model.[3,7–9] In view of the large bending angle of the Pb_2^{3+} (STEL) center, the use of the linear molecular model and the resulting values of the excitation energies E_{1g} and E_{2g} and of the hf contributions ρ_s and A_σ should be considered, at the very best, a crude approximation. Unfortunately, the neglected additional contributions to both g and A hf tensors resulting from the bending effects could be important, but are difficult to estimate without tedious calculation. However, the close values of the resulting crystal field splittings and hf contributions for the STEL center, calculated with the linear molecular model (Table I of Ref. 1), compared to those of the isoelectronic Pb_2^{3+} centers in NaCl, suggest that such an analysis may be employed, with caution, in a semiquantitative manner.

Using the linear molecular model, with the same approximations employed in the previous papers[7–9] we estimated, from the ESR parameters determined at $T = 10$ K and $T = 78$ K, the corresponding separations between the σ_g ground level and the π_g^x and π_g^y excited levels E_{1g} and E_{2g}, respectively, as well as the anisotropic ρ_s and isotropic A_σ hf contributions. The values of $E_{1g} = 1.22$ eV and $E_{2g} = 3.38$ eV, determined at $T = 10$ K, are comparable to the corresponding values[8] for the Pb_2^{3+} centers in NaCl. The determined decrease of both excitation energies, about 0.2 eV from 10 to 78 K, is due to a decrease in the crystal field component along the a direction. The observed temperature variation of the hf tensor components A_i is determined by the variation of the isotropic hf tensor component A_σ (Fig. 3). As expected, the hf anisotropic contribution $\rho_\sigma = 27$ mT of the STEL center in $PbCl_2$ has been found to be positive, comparable to the corresponding values ($\approx$30 mT) for the linear Pb_2^{3+} centers[8] in NaCl, and almost constant in the whole measured temperature range, reflecting its $\langle r^{-3}\rangle_s$ dependence, which is to a considerable degree independent of the crystal lattice host.[12,13] The analysis of the A_i hf tensor components with the molecular model shows that the variation of the isotropic A_σ contribution is mainly due to a decrease in the Fermi term A_σ^s from 52 mT at 10 K to 48 mT at 78 K. Such a variation corresponds to a decrease of the 6s wave function density at the Pb nuclei, which could be induced by an increase in the molecular bond length.

Although very limited in its accuracy, the above mentioned analysis of the temperature variation of the ESR parameters with the linear molecular model suggests a stronger coupling of the STEL center to the $PbCl_2$ lattice, compared with the linear Tl_2^+ and Pb_2^{3+} molecular centers in alkali halides, which may be due to its bent structure, as well as to the anisotropic thermal expansion of the crystal lattice.

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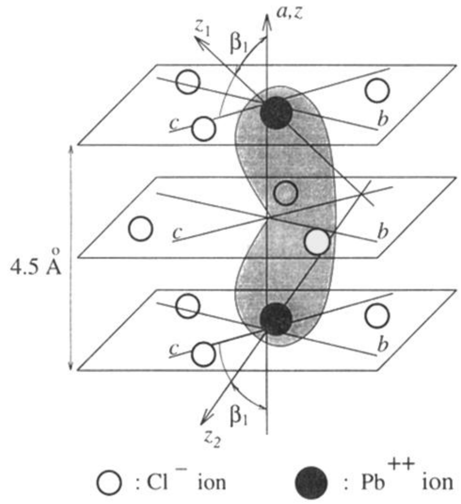

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