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MODELING OF NONLINEAR OPTIC AND ESR RESPONSE OF CDW MX MATERIALS

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We report results on the nonlinear optic and ESR response of the PtX MX chain materials calculated using a discrete, 3/4-filled, two-band, tight-binding Peierls-Hubbard model. We calculated electroabsorption (EA) spectra for the three PtX (X=Cl, Br, I) charge-density-wave (CDW) materials and find good agreement with the experimental data. We also obtain EA spectra for localized defects in PtBr. In addition, the field orientation dependence of the electron spin resonance spectra associated with the spin carrying defects is calculated for PtX materials and compared with ESR data on photoinduced defects.

I. INTRODUCTION

Halogen-bridged mixed-valence transition metal linear chain complexes (or MX chains, M: Pt, Pd, Ni; X: Cl, Br, I) are highly anisotropic, quasi-one-dimensional materials with competing electron-phonon and electron-electron interactions. By changing metal (M=Pt, Pd, Ni), halogen (X=Cl, Br, I) and ligands (X, ethylamine, ethylenediamine, cyclohexanediamine) attached to the metals, the physical properties of MX materials can be tailored almost continuously.

Here we focus on the theoretical predictions of the two-band model¹ (discussed below) for (i) the electroabsorption (EA) and (ii) magnetic field orientation dependence of electron spin resonance (ESR) spectra in pure MX materials both in the ground state and upon chemical or photo-doping. Electroabsorption is an important measurement for photo-refractive materials that provide many nonlinear optical applications for signal processing, e.g. real-time holography, dynamic interconnection, and optical memories. It is worth noting that certain defect states, e.g. excitons, are inaccessible via impurity doping, but may be obtained during photoexcitation. This situation is illustrated below for a triplet exciton. Results for the strongly localized material PtCl are contrasted with weakly localized materials, PtBr and PtI.

The ESR evidence for a localized paramagnetic defect with spin density extended over several platinum sites in PtX was known two decades ago. However, the first attempt to detect the unpaired electron state in PtCl via ESR was reported more than a decade ago by Aoki et al.² Since then several careful experimental studies have now established³ that the spin density is predominantly spread over two neighboring Pt atoms on the chain (origin of the hyperfine splitting) with the remaining spin density on Cl ions between and around the two Pt atoms (origin of the superhyperfine splitting). However, the nature of the spin carrying defect, i.e. whether it is a neutral soliton or a polaron or a triplet exciton, is not

well understood and the issue is far from resolved. We have reported the ESR spectra of the spin carrying defects previously⁴. Here we discuss the dependence of the ESR spectra on the orientation of the magnetic field with respect to the chain axis.

II. MODEL

To model these materials we focus on the metal d_{z^2} and halogen p_z orbitals and include only the nearest neighbor interactions. We construct the following *two band* tight-binding many-body Hamiltonian¹:

$$H = \sum_{l\sigma} (-t_0 + \alpha \Delta_l) (c_{l\sigma}^\dagger c_{l+1\sigma} + c_{l+1\sigma}^\dagger c_{l\sigma}) + \sum_{l\sigma} [\epsilon_l - \beta_l (\Delta_l + \Delta_{l-1})] c_{l\sigma}^\dagger c_{l\sigma} + \sum_l U_l n_{l\uparrow} n_{l\downarrow} + \frac{1}{2} \sum_l K_l \Delta_l^2 + \frac{1}{2} \sum_l K_{MM}^l (\Delta_{2l} + \Delta_{2l+1})^2. \quad (1)$$

Here $c_{l\sigma}^\dagger$ ($c_{l\sigma}$) denotes the creation (annihilation) operator for the electronic orbital at the l th atom with spin σ . M and X occupy even and odd sites, respectively. $\Delta_l := \hat{y}_{l+1} - \hat{y}_l$, where $\hat{y}_l$ are the displacements from uniform lattice spacing of the atoms at site l . Eq. (1) includes as parameters the on-site energy or electron affinity ϵ_l ($\epsilon_M = e_0$, $\epsilon_X = -e_0$), electron hopping (t_0), on-site (β_M, β_X) and inter-site (α) e -ph coupling, on-site e - e repulsion (U_M, U_X), and finally effective M - X (K) and M - M (K_{MM}) spring constants to model the elements of the structure not explicitly included. In particular, K_{MM} accounts for the (halide-dependent) rigidity of the metal sublattice connected into a 3D network via ligands. Periodic boundary conditions are employed with chain length of $4n$ sites, where n is an integer. Other boundary conditions, such as antiperiodic and open chain, were also used in certain test cases and did not seem to affect the results

in any significant manner, except to tend to center the defects at, or maximally away from, the boundary.

At stoichiometry there are formally 6 electrons per M_2X_2 unit, i.e., 3/4 band filling. A combination of ground state experimental data, quantum chemical and band structure calculations have led us to the effective parameter sets for the Hamiltonian, Eq. (1), listed in Table I.

III. NLO RESPONSE: ELECTROABSORPTION

The calculated third harmonic generation (THG) or χ^3 spectra for PtCl, PtBr and PtI have been described and compared with experimental data on PtCl in Ref. 5. Here we discuss the calculated electroabsorption spectra for PtX materials. In the presence of an electric field F , we add the term $-F \sum_i e r_i$ to Hamiltonian (1), fix the same lattice configuration, and recalculate the absorption, $\alpha(\omega)$, using the same lattice configuration as $F = 0$. The electroabsorption is then obtained as $\Delta\alpha(\omega) = \alpha(\omega, F) - \alpha(\omega, 0)$, i.e. non-perturbatively. It is found that the absorption edge red-shifts, while the absorption maximum blue-shifts with electric field. We note that for 3D semiconductors the electric field induced linewidth broadening of EA varies as $F^{2/3}$ (the Franz-Keldysh effect⁶). Franz and Keldysh assumed that the crystal field effect is included via the effective mass of electrons and holes, which is taken to be constant even in the presence of the electric field. Then analytic EA expressions are possible and the broadening and oscillation of EA are proportional to $(F^2/m^*)^{1/3}$, where m^* is the effective mass. The assumption of constant effective mass appears to be invalid for the PtX chains at low electric fields.

In Fig. 1 we present the calculated EA spectra for the three PtX materials with varying strength of the CDW: Strong for PtCl (Peierls gap = 2.5 eV), moderate for PtBr (gap = 1.45 eV) and weak for PtI (gap = 1.1 eV). We have chosen a field value $F = 200$ kV/cm and a small broadening $\eta = 0.05$ eV. The calculated spectra are in good agreement with the experimental spectra of Wada and Yamashita⁷ obtained by Kramers-Kronig transformation of the reflectivity data. We calculated the EA spectra for various field values and did not find any definite energy shift in the EA structures due to variation in the strength of applied electric field. This is consistent with the experimental observation⁷ that at low field values the mechanism of electromodulation does not follow the Franz-Keldysh effect.

In Fig. 2 we depict the EA spectra for bipolaronic defects for the intermediate strength CDW material PtBr for rescaled parameter values (with a Peierls gap of 1.95 eV instead of 1.45 eV) for illustrative purposes. We have chosen $F = 300$ kV/cm and $\eta = 0.03$ eV for demonstrating the intragap EA structures due to localized defects. The band states are very similar for the electron and hole bipolarons as well as for the exciton. However, the intragap features are very different indicating the asymmetry inherent in the two-band model. The intragap features are particularly pronounced for the exciton whereas they are weak for the hole bipolaron. The location of intragap features is also very different. The calculated spectra for solitonic and polaronic defects have been discussed in Ref. [5]. The features above the Peierls gap are due to electromodulation of X to M band transitions. It would be most interesting to observe these features experimentally.

IV. FIELD ORIENTATION DEPENDENCE OF ESR

The spin Hamiltonian for an electron with spin S in an external magnetic field H is given by:

$$H = -g_e H \cdot S + H_{int}, \quad (2)$$

where $g_e = 2.00232$ (for a free electron) and H_{int} is described below.

The splitting of the resonance line into several lines due to the hyperfine interaction, i.e. the coupling of the electronic spin with the nuclear spin, is given generally by the following Hamiltonian:

$$H_{int} = \frac{8\pi}{3} g_e g_N \vec{I} \cdot \vec{S} |\Psi(0)|^2 + g_e g_N \int \frac{\hbar^2}{r} \left[\frac{3(\vec{I} \cdot \vec{r})(\vec{S} \cdot \vec{r})}{r^2} - \vec{I} \cdot \vec{S} \right] |\Psi(\vec{r})|^2 d\vec{r}, \quad (3)$$

where $|\Psi(\vec{r})|^2$ is the density of unpaired electrons at position $\vec{r}$, g_N is the nuclear g-factor, and $\vec{I}$ denotes the nuclear spin. The first term of the interaction Hamiltonian is called the contact term and produces a field at the nucleus from the contributions of electrons with s-character. To evaluate this term we have used the charge density $\rho^\uparrow(0) - \rho^\downarrow(0)$ as obtained from our local density approximation (LDA) in conjunction with the linear muffin-tin orbitals in the atomic sphere approximation⁸ (LMTO-ASA) for the electronic structure calculation of PtX (X=Cl, Br, and I). Our calculations, however, have

TABLE I. Representative parameters for the PtX materials in Eq. 1. E_g is the IVCT band edge, and $\beta_X = -0.5\beta_M$.

MX	$\Delta(\text{\AA})$	$E_g(\text{eV})$	$t_0(\text{eV})$	$\alpha(\text{eV/\AA})$	$e_0(\text{eV})$	$\beta_M(\text{eV/\AA})$	$U_M(\text{eV})$	$U_X(\text{eV})$	$K(\text{eV/\AA}^2)$	$K_{MM}(\text{eV/\AA}^2)$
PtCl	0.38	2.50	1.02	0.5	2.12	2.7	1.9	1.3	6.800	0.0
PtBr	0.24	1.56	1.26	0.7	0.60	1.8	0.0	0.0	6.125	0.7
PtI	0.12	1.10	2.45	2.53	0.10	0.51	0.0	0.0	7.420	0.5

FIG. 1. Theoretical EA spectra (arb. units) for the three CDW materials (a) PtCl, (b) PtBr, and (c) PtI.

FIG. 2. Theoretical EA spectra (arb. units) for bipolarons in the intermediate strength CDW material PtBr: (a) Electron bipolaron, (b) hole bipolaron, and (c) exciton.

FIG. 3. Predicted field orientation dependence of the ESR spectra of a triplet exciton on a PtCl chain for the polar angle (a) $\theta=0^\circ$, (b) $\theta=45^\circ$, and (c) $\theta=90^\circ$.

shown that this term is negligible in comparison to the second term in Eq. 3.

In Fig 3 we depict the field orientation dependence of a triplet exciton for three different values of the field angle. The five-peak hyperfine structure arises from most of the spin density (from two parallel spins) spread over two neighboring Pt ions. The superhyperfine structure results from the remaining spin density distributed over three Cl ions around and between the two Pt ions⁴. Note that with increasing angle the five-peak structure persists but the superhyperfine structure diminishes. In other words, the relative magnitude of the spin density on the halogen sublattice decreases with increasing angle. The peak-to-peak intensity of the ESR signal (I_{pp}) increases almost linearly with the field orientation angle (θ). These results are consistent with the experimental observation of Kuroda et al.³ although we do not claim here that the experimental spectra can be attributed to a triplet exciton.

V. CONCLUSIONS

We have presented examples of theoretically calculated EA and field orientation dependence of ESR spectra for doping- and photo-induced defects in PtX materials with differing strength of CDW. Investigations of the influence of Coulomb interactions (both on-site and inter-site Hubbard terms) are in progress on EA and ESR studies of pure as well as mixed-halide MX materials. The computation of χ^3 for various nonlinear excitations (solitons, polarons, etc.) and the second order nonlinear optical susceptibility (χ^2) for mixed-halide ($\text{PtCl}_x\text{Br}_{1-x}$) materials, which lack centrosymmetry, is also underway. For the whole MX and related classes of materials, NLO and ESR, taken together with optical absorption and phonon experimental data should provide stringent tests of the reduced many-body model Hamiltonian discussed above, as well definitive "labels" for the various doping and photo-induced defects: Understanding these local excitations is critical to functionalizing the materials for device applications.

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