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Characterization and Manipulation of Broken Symmetry Materials at Phase Boundaries

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Abstract

This is the final report of a three-year, Laboratory Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). The ability to control the electronic properties of strongly correlated electronic materials (materials that exhibit electronic structure that is dominated by the lattice nuclei) will include observation and manipulation of phase transitions. Low dimensional materials represent one class in which both charge density wave (CDW) and spin density wave (SDW) ground states can be observed. This project had two major goals: to observe the inelastic (magnon) scattering from low dimensional SDW materials and to characterize magnetic defects within a CDW lattice. Toward these ends, we developed the capability of monitoring Raman spectra for weak CDW materials and SDW materials in high magnetic fields and also used isotopic enrichment to characterize the spatial extent of spin density in some photo-irradiated CDW samples. No magnon signatures or field-induced phase transitions were observed. Detailed spatial and dynamics characteristics of photo-induced magnetic defects in CDW samples were obtained.

Background and Research Objectives

Field-induced effects in weak CDW materials have been reported in the literature. In one instance, a low-dimensional platinum-iodide "MX" chain has been observed to exhibit approximately 76% of perfect diamagnetism under applied magnetic fields.¹ This high degree of diamagnetism is reminiscent of the nearly perfect diamagnetism exhibited by many superconductors. Thus, the influence of applied magnetic field on the ground and defect states of low-dimensional materials is of interest as a means of controlling electronic structure. Theoretical and experimental characterization of MX chains such as $[\text{Pt}^{\text{IV}}(\text{en})_2\text{I}_2][\text{Pt}^{\text{II}}(\text{en})_2(\text{ClO}_4)_4]$, where en=ethylenediamine, referred to hereafter as PtI, has demonstrated that it lies at the weak end of the spectrum of low-dimensional CDW materials. In other words, the broken symmetry CDW ground state in the MX materials, which includes disproportionation of electronic charge among the metal sites and a commensurate dimerization of the halide sublattice, is only weakly stabilized relative to

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other possible ground states. These other possibilities include a metallic state or, much more likely, other insulating states such as the SDW or spin-Peierls phases. Such magnetic ground state structures have been reported for NiBr, another member of the MX class.

One potential experimental probe of the SDW phase is magnon scattering. In this phenomenon, which is similar to Raman scattering, inelastic scattering of incident (laser) light can yield signatures that are indicative of exchange energies, exchange anisotropies, g factors, and other magnetic properties of SDW phases.² Our objective in this LDRD project included the search for such magnon signatures in PtI and NiBr under applied magnetic fields.

In addition to phase transitions, the MX materials often exhibit stabilized magnetic defects within a CDW matrix. The nature of these defects, which can be intrinsic or induced, has been the subject of controversy. Theoretical and experimental descriptions of such states have argued both in favor of neutral magnetic defects such as kinks³ and charged magnetic defects such as polarons.⁴ The identification of the precise nature of these defects is of importance because the relaxation pathways following photoexcitation reveal a great deal regarding the nonlinear physics in correlated materials. Thus, how an excited state emits localized and extended perturbations within the lattice as it relaxes will profoundly influence the ultimate character of such metastable sites as polarons and solitons. As a means of characterizing these defects, we pursued an intensive examination of the electron paramagnetic resonance (EPR) spectra of photoinduced defects in a strong CDW material, PtCl. By enrichment of the metal, halogen, and ancillary ligand isotopic compositions, we sought to firmly identify the magnetic defects.

Importance to LANL's Science and Technology Base and National R&D Needs

The ability to dynamically control materials structure and properties is emerging as a central theme in development of the next generation of materials. Sensors, nonlinear optics, photo-sensitive switches, molecular electronics, and biomimetic materials all include development-phase and final product systems that function on a variety of temporal and spatial scales. For electronic materials in particular, this control of scale includes a requirement of manipulating the structures of ground and local or defect states. Thus, the central importance of the theme underlying the present research project for national and LANL science and technology is clear.

In addition to general materials issues, specific capabilities within LANL also influenced the direction and success of this project. Our ability to couple the extensive optical spectroscopic probes and synthetic chemistry capabilities with the National High

Magnetic Field Laboratory (NHMFL) allowed us to be self sufficient in our search for magnon signatures from weak CDW and SDW materials under fields. The stable isotope chemistry capabilities permitted our search for defect-specific signatures in the EPR spectroscopy of photo-irradiated CDW samples. Finally, extensive and regular interactions with our colleagues in condensed matter physics allowed us to interpret and direct some of our experimental efforts by application of codes specifically designed to explore the coupling of lattice, charge, and spin energies in low dimensional materials.

Scientific Approach and Accomplishments

By a classic theorem due to Peierls,⁵ symmetric low-dimensional materials tend to be unstable with respect to distortions of the lattice and electronic structure, leading to lowered symmetry and the formation of electronic gaps. MX chains, with alternating platinum group metals (M) and halogens (X) typically adopt the broken symmetry CDW ground state. This structure can be conceptualized as a series of metal centers with alternating reduced and oxidized character, tending toward +2 and +4 in charge. The halogen nuclei dimerize toward the oxidized site, and the degree of dimerization, along with the extent of the charge disproportionation within the metal sublattice, is a measure of the CDW strength. The scientific approach toward identification of field-induced phase transitions in weak CDW materials was based on the magnetization data for PtI. PtI has a low energy gap (~ 1 eV) and weak dimerization of the halide sublattice. As noted above, PtI exhibits a strong tendency toward increased diamagnetism under applied magnetic fields. Around 7 T, Haruki *et al.* observed that PtI exhibited an apparent phase transition toward a highly diamagnetic structure.¹ This observation raised the exciting possibility that phase transitions could be field-induced in the low dimensional materials.

We have routinely used Raman spectroscopy as a probe of the electronic structure of MX materials.⁶ The dimerized halide sublattice leads to a characteristic symmetric halogen stretching mode for MX chains that can be observed by inelastic scattering of intense, monochromatic (laser) light. The characteristic Raman band for MX materials has long been used in our laboratory to explore correlation lengths, CDW strength, defect formation, and other characteristics of the MX materials via Raman spectroscopy. Thus, our challenge to search for phase transitions in MX materials under magnetic fields was approached by incorporation of laser-based optical spectroscopic measurements into the NHMFL. This involved a fair amount of facilities engineering and training, which was graciously aided by the personnel in the NHMFL, especially Dwight Rickle and Alex Lacerda. The moving and installation of lasers, heat exchangers, optics and optical fibers

into the vicinity of the 20 T magnet posed a significant barrier to this project that would not have succeeded without the full cooperation and support of NHMFL personnel.

Unfortunately, our hoped-for phase transitions did not appear as any clearly observable effect on the Raman data from PtI. Some evidence for a broad band, possibly a magnon state, near 1500 cm^{-1} was observed in some samples, but not in every case. Further, the photolysis of stronger CDW materials, which is known to yield magnetic defects, did not reveal any field-dependent Raman modes despite such modes being clearly associated with the magnetic defects. Finally, we sought for magnon signatures in SDW MX chains such as NiBr and did not detect any such transitions. While we have to this point failed in our efforts to detect field-induced phase transitions by this approach, we have not yet abandoned hope for our project. In order to more firmly correlate magnetization and optical data, we have designed a combined susceptibility/fiber optic Raman probe that can allow us to unequivocally detect any transitions such as those described in the literature and correlate any corresponding optical signals.

In contrast to the NHMFL experiments, our efforts to identify photoinduced paramagnetic defects in CDW materials has been highly successful. PtCl is a strong CDW material that is not paramagnetic in its ground state. Upon illumination above the band gap (around $\sim 2.4\text{ eV}$), charge transfer from the reduced to the oxidized sites is initiated (over how many sites is an issue for theory and experiment, but in general such excitations are highly localized in a strong CDW materials and delocalized in weak CDW samples). At low temperatures, the charge separated exciton decays to the ground state or to metastable defects. Conceptually, the ground, polaron, and kink sublattices may be represented as follows, where the numbers refer to the approximate oxidation state of the Pt site and the X to the halide location:

X	2	X	4	X	2	X	4	X	2	X	4	X	2	X...	Ground State
X	2	X	4	X	2	X	3	X	2	X	4	X	2	X...	Electron Polaron
X	2	X	4	X	2	X	4	X	3	X	4	X	2	X...	Hole Polaron
X	2	X	4	X	2	X	3	X	4	X	2	X	4	X...	Kink

Note the reversal of phase of the CDW in the kink defect, and the fact that the polarons represent charged defects while this form of kink is neutral. A powerful spectroscopic probe of such paramagnetic defects has been EPR. Our singular success in this arena, where numerous research groups around the world have contributed, is due to our efforts to generate isotopically enriched samples. Until now, interpretation of the EPR data from photolyzed samples of PtCl has been confused in part by the many hyperfine interactions, which can arise from spin density on the Pt sites, the Cl sites, and, conceivably, the chelating N sites from the equatorial (off-chain) ligands. Each of these nuclei has multiple

isotopes which have differing magnetic properties. ^{195}Pt , for example, is approximately 33% abundant in nature and has a nuclear spin of $1/2$ while other naturally occurring Pt isotopes are spinless. Both ^{35}Cl (76% natural abundance, N.A.) and ^{37}Cl (24% N.A.) have a nuclear spin of $3/2$, but the magnetogyric ratio of the latter is 83% that of the former, thereby affecting the extent of coupling to an unpaired electron spin. Conversely, while Pt and Cl have a variety of hyperfine interactions, N has one primary N.A. isotope (14) with nuclear spin $I=1$. Consequently, synthesis of PtCl with its ancillary ligands (for example, ethylenediamine) substituted with ^{15}N , $I=1/2$, should profoundly influence any observable hyperfine interaction arising from these nuclei.

The literature EPR data for paramagnetic defects in PtCl reveal that the spin is delocalized over two Pt sites.³ The result is a five-line pattern, over which further hyperfine signatures are distributed in a convolved manner. To simplify the EPR data we examined samples of $^{194}\text{PtCl}$, and $^{194}\text{Pt}^{37}\text{Cl}$. Spectra were obtained at a variety of orientations between 0° and 90° . The following results were obtained:

- The so-called 16G superhyperfine pattern that has been attributed to the participation of ^{14}N is instead clearly due to Cl. As shown in Fig. 1, the collapse in the superhyperfine splitting upon substitution of the N.A. Cl with ^{37}Cl was exactly commensurate with the expected change in magnetogyric ratio and indeed revealed that the spectrum is fundamentally comprised of features due to Cl splitting of the Pt-split EPR pattern. This was verified by examination of PtCl synthesized with ^{15}N , where no influence of this substitution on the EPR pattern was observed.
- The evolution of the EPR spectrum from 0° to 90° (g parallel to g perpendicular) is not easily explained by the polaron model of the defect but is similar to the expectations derived from a kink model of the defect.
- A novel form of dynamic behavior occurs below 6K, where the defect EPR spectrum is altered in lineshape. This is clearly not an activation of the defect but may arise due to oscillations of the spin between the two Pt lattice sites on the timescale of the EPR measurement.
- In addition to the photoinduced kink, a variety of additional EPR signatures were observed for some samples. One is likely a spin triplet and the other appears at elevated temperatures and is metastable at room temperatures.

Publications

1. Wei, X., Johnson, S. R., Swanson, B. I., Donohoe, R. J., "ESR study of isotopically enriched quasi-one-dimensional chlorine-bridged platinum complexes," *Phys. Rev. B*, **56**, 8257-8264 (1997).
2. Saxena, A., Shuai, Z., Gammel, J. T., Batistic, I., Alouani, M., Bredas, J. L., Bishop, A. R., "Modeling of nonlinear optic and ESR response of CDW MX materials," *Synth. Metals* **71**, 1659-1662 (1995).
3. Zang, J., Roder, H., Gammel, J. T., Saxena, A., Bishop, A. R., "Phonon effects in the two-magnon Raman scattering in spin-peierls systems," *Synth. Metals* **86**, 2227-2228 (1997).
4. Scott, B. L., Love, S. P., Kanner, G. S., Johnson, S. R., Wilkerson, M. P., Berkey, M., Swanson, B. I., Saxena, A., Huang, X. Z., Bishop, A. R., "Control of selected physical properties of MX solids: an experimental and theoretical investigation," *J. Mol. Struct.* **356**, 207-229 (1995).

References

- [1]. Haruki, M., Wachter, P. "Magnetic-field-induced strong diamagnetic transition in the quasi-one-dimensional halogen-bridged platinum complex $\text{Pt}(\text{en})_2[\text{Pt}(\text{en})_2\text{I}_2](\text{ClO}_4)_4$," *Phys. Rev. B* **43**, 6273-6276 (1991).
- [2]. Chubukov, A. V., Frenkel, D. M., "Resonant two-magnon scattering in antiferromagnetic insulators," *Phys. Rev. Lett.* **74**, 3057-3060 (1995)
- [3]. Sakai, M., Kuroda, N., Suezawa, M., Nishina, Y., Sumino, K., Yamashita, M., "ESR study on local structure of UV-induced midgap states in $[\text{Pt}^{\text{IV}}(\text{en})_2\text{Cl}_2][\text{Pt}^{\text{II}}(\text{en})_2](\text{ClO}_4)_4$," *J. Phys. Soc. Jpn.*, **61**, 1326-1335 (1992)
- [4]. Arrington, C. A., Unkefer, C. J., Donohoe, R. J., Hockett, S. C., Kurita, S., Swanson, B. I., "On the origin of the hyperfine structure in the photoinduced EPR spectrum of $[\text{Pt}^{\text{IV}}(\text{en})_2\text{Cl}_2][\text{Pt}^{\text{II}}(\text{en})_2](\text{ClO}_4)_4$," *Solid State Commun.*, **84**, 979-984, (1992).
- [5]. See H. J. Keller, in *Extended Linear Chain Compounds*, edited by J. S. Miller (Plenum, New York, 1983), vol. 1, p. 357.

Figure 1. The comparative LESR spectra of $^{194}\text{Pt-Cl}$ (solid lines) and $^{194}\text{Pt-}^{37}\text{Cl}$ (dashed lines) at $g_{//}$ and $g_{\perp}$, respectively. The integrated ESR spectra are plotted here to emphasize the overall spectral width variations upon chlorine isotope substitution. The superhyperfine splitting is also seen to vary.