Phase separation in the non-equilibrium Verwey transition in magnetite

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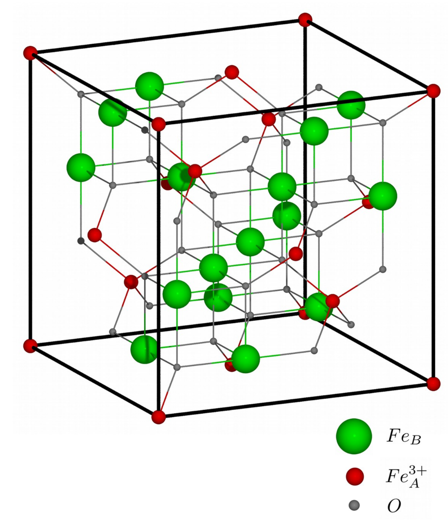
ABSTRACT

The possibility of triggering a non-equilibrium transient metallic state in insulating magnetite by photo-excitation was recently demonstrated by an x-ray study [1]. We studied the optical properties of magnetite both at equilibrium and out-of-equilibrium after photo-excitation. The out-of-equilibrium optical data bear the initial electronic response associated to localized photo-excitation, the occurrence of phase separation, and the transition to a transient metallic phase for excitation density larger than a critical value.

WHY THE VERWEY TRANSITION?



Verwey insulator-to-metal phase transition at $T_V = 123$ K.

High temperature phase:
- Inverse spinel structure
- A and B sites for Fe ions
- A sites: Fe_A^{3+} with d orbitals occupied by ↓ spins
- B sites: random distribution of

	Fe_B^{3+}	Fe_B^{2+}
d-orbitals	5 ↑	5 ↑ 1↓

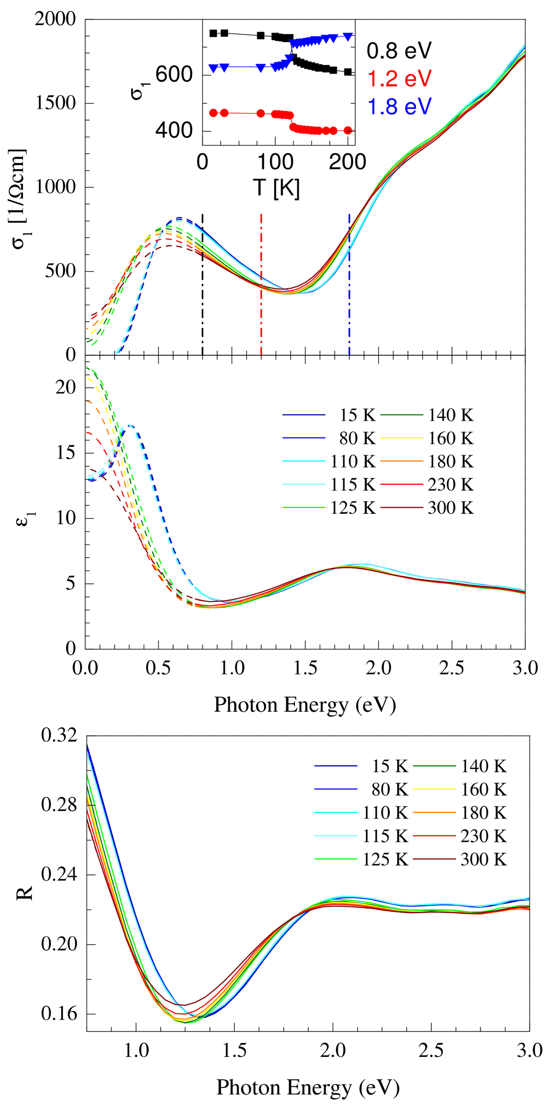
Low temperature phase [2]:

Charge ordering on the B sites

The Verwey transition is the ideal playground to study out-of-equilibrium phase transitions (clear variation of the optical properties at the transition).

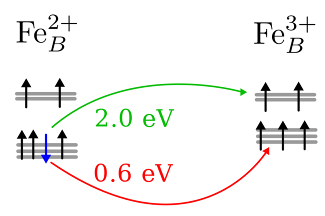
EQUILIBRIUM AND OUT-OF-EQUILIBRIUM OPTICAL PROPERTIES

Equilibrium

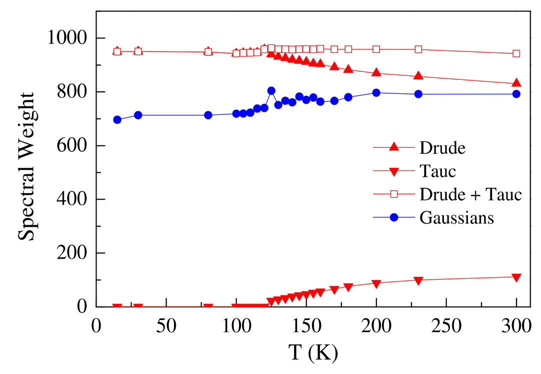


Relevant excitations [3]:

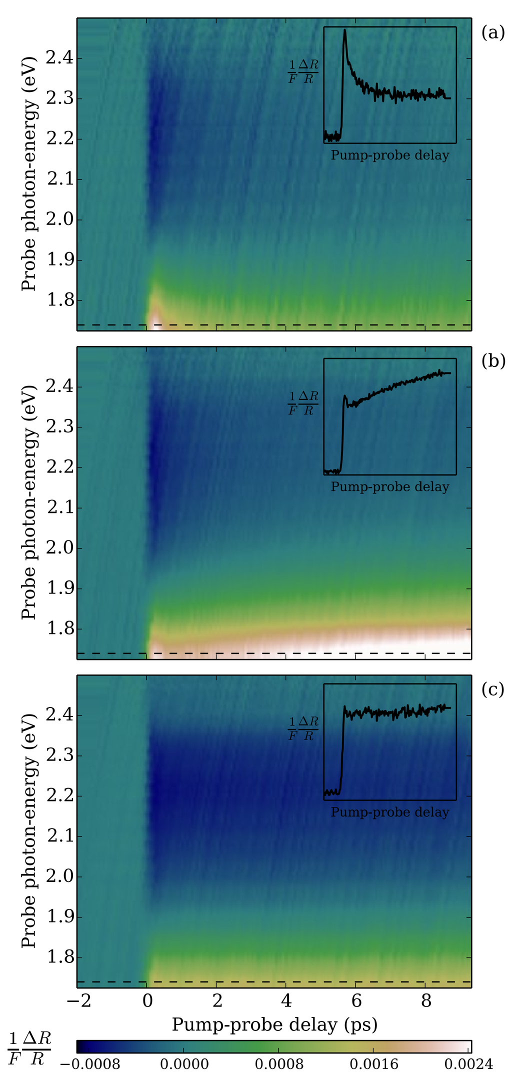
- 0.6 eV $Fe_B^{2+} t_{2g} \downarrow \rightarrow Fe_B^{3+} t_{2g} \downarrow$
- 2 eV $Fe_B^{2+} t_{2g} \downarrow \rightarrow Fe_B^{3+} e_g \downarrow$



Entering charge-order:
- 0.6 eV gains spectral weight
- 2 eV loses s.w.



Out-of-equilibrium $\frac{\Delta R}{R}(t, h\nu)$



Three pump-fluence regimes

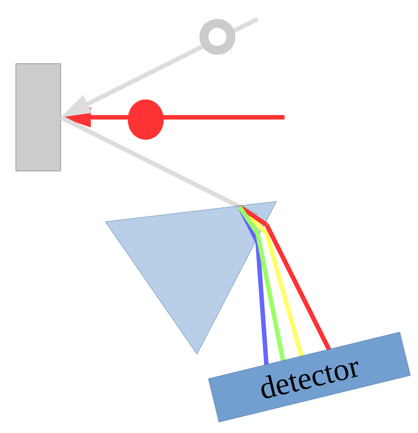
Low fluence $F < F_1$
- Fast response decaying to thermal plateau
- Linear with fluence

→ Local destruction of charge-order.

Sample below T_V
35, 80 K

Intermediate fluence $F_1 < F < F_2$
- Fast response (scales linearly with F)
- Additional slow response (non-linear with F)

A sufficient number of excitations triggers a new dynamical response. → Nucleation of the metallic phase.

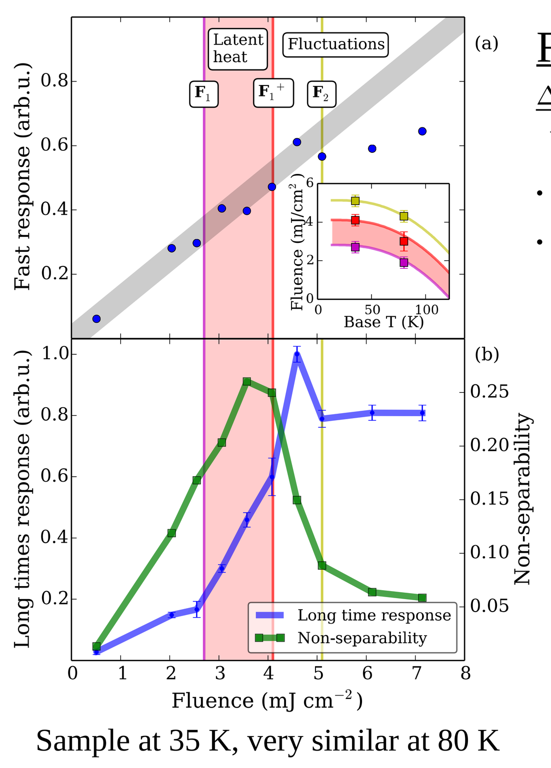


High fluence $F > F_2$
- Loses the above mentioned features.
- Almost switch-like with no evolution.

→ Immediate transition to the metallic phase.

PHASE TRANSITION DYNAMICS

Where to look for phase separation?
Out-of-equilibrium phase transition and its relation to equilibrium



Sample at 35 K, very similar at 80 K

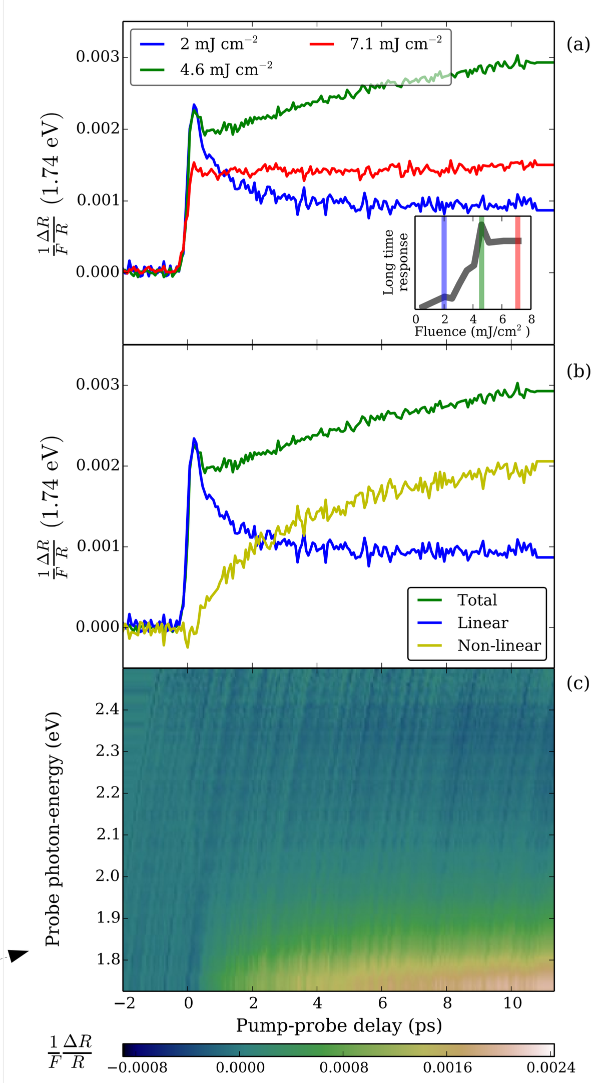
Fast response
$\frac{\Delta R}{R}|_{1.7\ eV}(0.2\ ps)$
- $F < F_2$ Linear with F
- $F > F_2$ Saturation

Long-time response
$\frac{\Delta R}{R}|_{1.7\ eV}(8\ ps)$
- $F < F_1$ Linear with F
- $F_1 < F < F_2$ Slow non-linear
- $F > F_2$ Saturation

Correspondence to equilibrium thermodynamics (inset)
- F_1 : 35 K → T_V^- (no latent heat)
- F_1^+ : 35 K → T_V^+ (full latent heat) see non-separability
- F_2 : 35 K → 140 K

Same for 80 K.

Out-of-equilibrium phase separation
and non-separability of the response



Intermediate fluence regime

$$\underbrace{\frac{1}{F}\frac{\Delta R'}{R}}_{\text{non-linear}} = \underbrace{\frac{1}{F}\frac{\Delta R}{R}}_{\text{total}} - \underbrace{\frac{1}{F_0}\frac{\Delta R}{R}\Big|_{F_0}}_{\text{linear}}$$

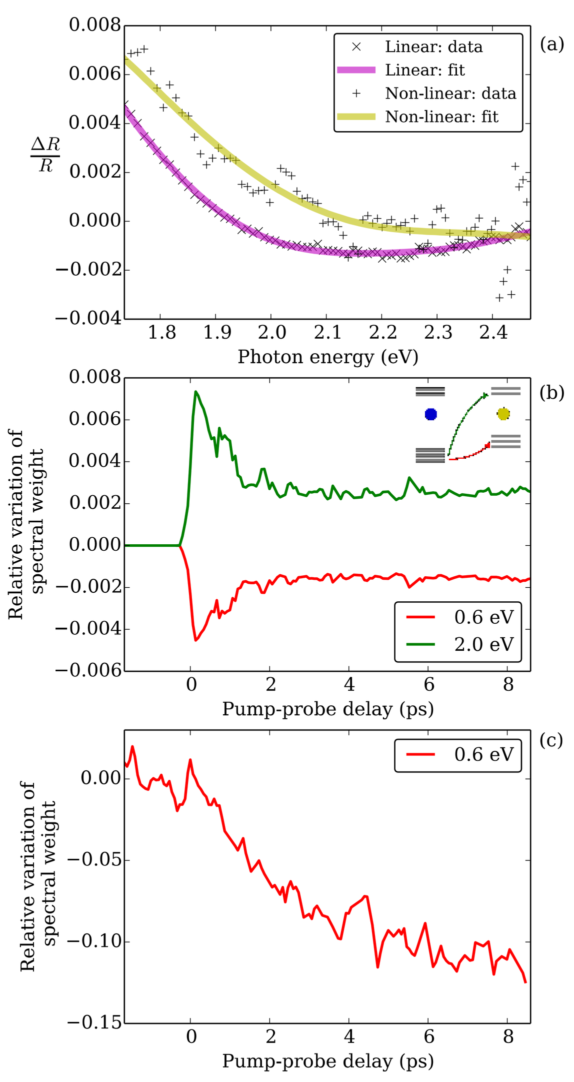
Non-linear part:
- $\frac{\Delta R}{R}(0.2\ ps)$ at all photon-energies → purely slow dynamics
- Timescale matches x-ray data in same excitation conditions [1]

R in the *intermediate* fluence regime is the *sum* of two terms with physical significance
→ *Phase separation*

Biased physical picture?
NO!: singular value decomposition tells us that $[\frac{\Delta R}{R}]|_{h\nu,t}$ is the furthest from being separable in the intermediate regime (← green curve).

Low and *high* fluence: **homogeneous** system
Intermediate fluence: out-of-equilibrium **phase separation**

The physical scenario
Spectral response of the nucleating metallic phase



Excitations involved in the dynamics
0.6 eV and 2 eV

Linear response
as heating at equilibrium

Nucleation of the metallic phase
Non-linear response: just 0.6 eV losing spectral weight

CONCLUSIONS

- Close to the threshold for the triggering of the photo-induced phase transition (intermediate fluence regime), out-of-equilibrium *phase separation* occurs in the system.
- The results of this work may have a general relevance for systems displaying photo-induced out-of-equilibrium first order phase transitions.
- A *non-separable dynamical response* may be a general fingerprint for out-of-equilibrium phase separation and a straightforward way to identify it.

[1] de Jong et al., Speed limit of the insulator–metal transition in magnetite, Nat. Mat. 12, 882–886 (2013)
[2] Senn et al., Charge order and three-site distortions in the Verwey structure of magnetite, Nature 481, 173–176 (2012)
[3] Leonov et al., Electronic structure of charge-ordered Fe_3O_4 ..., Phys. Rev. B, 74, 165117 (2006)