Names and affiliations of applicants (* indicates experimentalists):

Moshe P. Pasternak, Gregory Kh. Rozenberg
School of Physics and Astronomy, Tel Aviv University, ISRAEL

Report:

Structural properties of the antiferromagnetic insulator CuFeO$_2$ were studied by synchrotron x-ray diffraction to 41 GPa, using diamond anvil cells. Pressures were generated with a membrane-type diamond-anvil cell having anvils with 300-µm diam. culets, with He used as a pressure medium. Angle-dispersive mode high-pressure XRD studies were performed at the ID09A beam-line, diffraction images were collected with a MAR345 detector. The image data were integrated using the FIT2D program [1], and the resulting diffraction patterns were analyzed with the GSAS [2] program. Pressure was measured using the ruby fluorescence technique.

The low pressure (LP) phase of cupric ferrite (CuFeO$_2$) is hexagonal consisting of Cu^{1+}, O^{2-}, and Fe^{3+} layers; forming the symmetry group $R\bar{3}m$. The Fe^{3+} (S=5/2) layers are antiferromagnetically coupled, separated by nonmagnetic layers of Cu^{1+} (S=0) and O [3]. At ambient pressure spins are highly frustrated between neighboring layers as well as within layers but at ~18 GPa CuFeO$_2$ becomes a normal antiferromagnet [4]. At recent high pressure (HP) ^{57}Fe Mössbauer studies (P>18 GPa) [5] have shown two remarkable events: 1 – abrupt pressure-induced reduction of about 1/3 of the Fe^{3+} ions, and 2 – a nearly threefold increase in the ordering temperature T$_N$ of the Fe^{2+} sublattice as compared with the Fe^{3+} ones. A most plausible and consistent explanation is that at a critical $\Delta V/V_0$ a sharp overlap occurs between the cuprite's and the ferric ions bands resulting in the oxidation of part of the Cu^{1+}, namely:

$$\left[\overset{\text{Fe}^{3+}\text{ sublattice}}{Cu^{+1}(S=0),\ Fe^{3+}(S=5/2)} \right] \rightarrow \left[\overset{\text{Fe}^{2+},\,\text{Cu}^{2+}\text{ sublattice}}{Cu^{+2}(S=1/2),\ Fe^{2+}(S=2)} \right] \qquad (1)$$
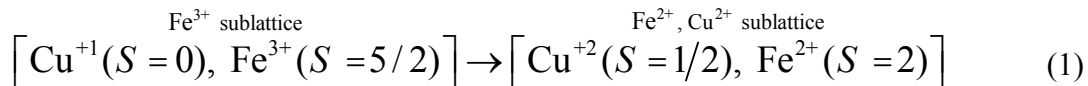
The presence of two paramagnetic ions, Fe^{2+} (S=2) and Cu^{2+} (S = 1/2) in the new formed magnetic sublattice with its enhanced T$_N$ will be consistent with the Fe$^{3+} \rightarrow$ Fe^{2+} mechanism.

Recent high pressure Cu and Fe K-edge XAS (Report #2185) provided additional experimental proof that indeed the process depicted in (1) is proper. Cu and Fe *K*- edge XANES shows a clear evidence of the Cu and Fe valence state changes at the 18 - 40 GPa pressure range: The energy position of the Cu absorption **increases** by ~1.5 eV while the Fe *K*-edge **decreases** nearly by the same (Fig. 1). Concurrent with the valence alterations the Cu EXAFS studies show significant changes of Cu-O distances and and of the Cu coordination number. This implies a structural phase transition corroborating the electronic transformation.

Representative diffraction patterns collected at the pressure range of 1.4 - 41 GPa are shown in Fig. 2. and the deduced pressure dependent molar volume is plotted in Fig. 3 [6]. The pressure-volume data fitted to the

third-order Birch-Murnaghan (BM) equation of state yields a bulk modulus of 148.0 (0.7) GPa, a pressure derivative $K_0' = 4$ (fixed), and a unit cell volume at 1 bar of V_0=136.93 (0.01) Å^3.

Two structural phase transitions are observed at the pressure range 18 -35 GPa in agreement with two distinct steps in the Cu K-edge shift observed at 21 GPa and ~ 30 GPa. The intermediate pressure (IP) phase (pressure range 18 - 28 GPa) can be well fitted with monoclinic (*Pnnm*) structure. This is also a layered structure but with bslightly distorted hexagonal structure. With further pressure increase (Pb>b30 GPa) the transition to a new high pressure (HP) phase takes place, characterized by a significant change of the Cu-environment characterized by the formation of distorted thetrahedra. This phase can be fitted well with monoclinic (*C12/m1*) structure which in contrast to the LP phase, accommodates two different types of Fe and Cu sites ($^1/_3$ of the Fe and Cu positions are occupied by Fe^{2+} and Cu^{2+} respectively). Both pressure-induced transitions are reversible in pressure.

A paper which will include the XRD, XAS and Mössbauer studies is now being prepared for publication.
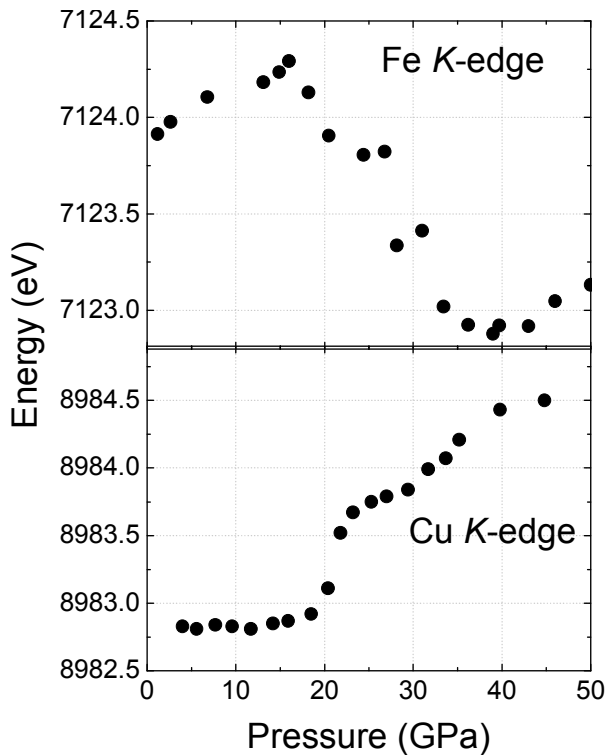

Fig.1. Evolution of the energy position of the X-ray absorption-onsets of Cu and Fe. The positive shift for Cu is related to modifications of $Cu^{1+} \rightarrow Cu^{2+}$, Fe shows a negative shift, consistent with $Fe^{3+} \rightarrow Fe^{2+}$.

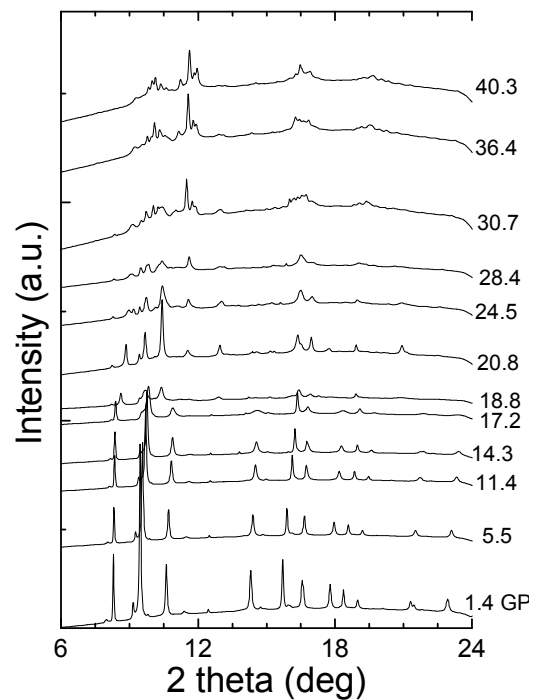Fig.2. X-ray powder diffraction patterns of $CuFeO_2$ at T = 298 K at various pressures.

References

1 - A. P. Hammersley, computer program FIT2D, ESRF, Grenoble, 1998.
2 - Larson A.C. *et al.*, Los Alamos National Laboratory, LAUR 86 (1994).
3 - A. Pabst, Am. Mineral, **75**, 105 (1988), M. Hasegawa, M. I. Batrashevich, T. R. Zhao, H. Takei, and T.Goto, Phys. Rev. B**63**, 184437 (2001).
4 - W.M. Xu, M.P.Pasternak, and R.D. Taylor, Phys.Rev B **69**, 052401, (2004).
5 - W.M. Xu *et al*, to be published.
6 - The narrow diffraction-line widths and excellent reproducibility of our measurements is a result of better hydrostatic conditions obtained by the He pressure medium.
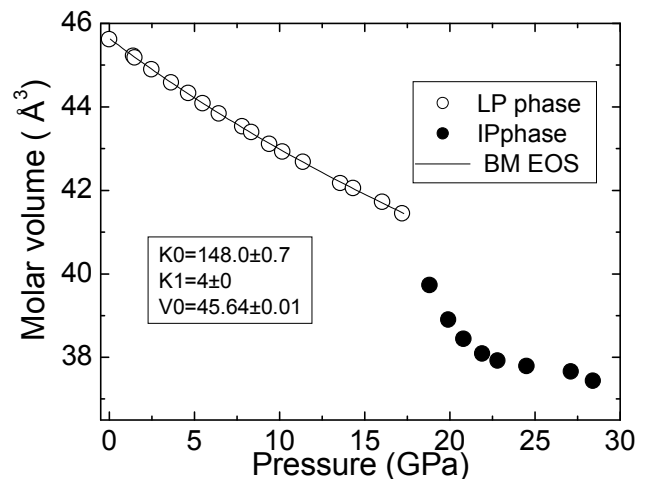
Fig.3. Pressure evolution of the unit cell volume of $CuFeO_2$.The solid line through the $V_M(P)$ ias a fit to the BM EOS.