Electron Paramagnetic Resonance of UO_{2+x}

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Introduction

UO_2, an industrial chemical that is the most common fuel for nuclear reactors, has recently been shown to display unusual collective properties. A $5f^2$, 2.2 eV gap Mott insulator that exhibits highly anisotropic thermal conductivity, it undergoes a spin-ordering transition at 30.8 K to a 3**k** AFM state concomitant with very small displacements of the O ions. It does, however, possess unusually large spin-phonon coupling that is manifested as the association of the spin with dynamic Jahn-Teller effects, low thermal conductivity, and its identification as the hardest piezoelectric material known [1]. It also possesses highly unusual dynamical electron-phonon coupling in its O-doped or photoexcited states, where the charge defects aggregate and self organize into a coherent polaron quantum phase (CPQP) that has been interpreted as a non-equilibrium condensate [2-4].

Below a few to several hundred °C the O in UO_{2+x} clusters so that for compositions between the single phase UO_2, U_4O_9, and U_3O_7 compounds the materials are intragranular mixtures of them. Susceptibility measurements show that 30.8 K AFM transition occurs at the identical temperature in $UO_{2.09}$ and $UO_{2.16}$ but that direction has inverted relative to UO_2. Furthermore, although the susceptibility of UO_2 is almost identical at both 0.1 and 5 T, the higher field strength eliminates the 30.8 K feature only for $UO_{2.08}$. X-band electron paramagnetic resonance spectroscopy was performed on these same samples [3]. All three samples showed three distinct behaviors in the temperature below 15 K, at 35-80 K, and above 90 K, with the two lower regions giving very similar results for each sample and UO_2 giving different results from the other two above 90 K. In addition, spectra measured through field reversal show not only that their value at 0 field is not zero but also hysteresis with some unusual characteristics that confirm the absence of ferromagnetism.

Experimental

Variable high field and conventional EPR measurements of $UO_{2.00}$, U_4O_9, and U_3O_7 were performed at NHFML using the 15/17 T SC magnet at the EMR Facility.

Results and Discussion

These measurements failed to reproduce the earlier results, yielding extremely weak spectra with some free electron-type and a few other unidentifiable signals. Discussions with collaborators for the previous measurements identified as the only difference that the original samples had been stored several months in a liquid N_2 refrigerator and that the signal continued to develop with further storage. Based on this, we hypothesize that the signals observed in the first measurement were caused by radiation effects that accumulated because of inhibited relaxation at the low storage temperature. When a sufficient threshold was attained these interacted to form metastable structures that gave the unusual EPR spectra. Although the essentially negligible radioactivity and correspondingly low defect concentrations of depleted uranium makes this process highly unlikely, we have no alternative explanations. The similarity in both the signal intensity and behavior precludes an oxidation-based process.

Conclusions

This hypothesis will be tested by repeating the measurements after a similar storage procedure, although, unlike the originals samples, the current ones were stored in an inert atmosphere glovebox for several months before being cooled.

Acknowledgements

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References:

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