

Solving a Historical Puzzle

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Abstract. We report x-ray absorption near edge structure (XANES) measurements of four closely related perovskite materials: SrTiO₃, CaTiO₃, CaZrO₃, and SrZrO₃. This data is used to address the conceptually important, early EXAFS experiment of Perel and Deslattes [1]. That experiment attempted to distinguish between the then-competing short-range and long-range theories of EXAFS by cross-material comparison of the EXAFS for the metal ions in the four perovskites reported here. Their inconclusive result is surprising, given the modern understanding of EXAFS. Our new measurements show strong disagreements with the prior results at multiple edges. When analyzed in qualitative, conceptual framework of the original study, our new results are in strong agreement with the short-range order theory. This solves a historical puzzle in the early scientific development of x-ray absorption spectroscopy.

Keywords: EXAFS, *history*

PACS: 61.10.Ht, 01.65.+g

INTRODUCTION

There ensued confusion for 40 years about the correct theory of the Extended XAFS (EXAFS) because two different theories were presented by Kronig between 1931- 1934: (1) the long-range order (LRO) [2,3] based on electron energy bands and gaps in solids; (2) the short-range order (SRO) [4] based on scattering of the photoelectron by neighboring atoms. Kronig proposed the LRO theory for periodic solids and the SRO theory for molecules. Although both theories, if properly performed, would give the correct answer for appropriate systems, we now know that his LRO theory had a fatal error, while his SRO theory was incomplete. The SRO theory did not include Debye-Waller factors, excited-state lifetime broadening, and the correct phase shift. Moreover, because no powerful computers existed then, the photoelectron-atom interaction could not be accurately calculated to allow quantitative comparison with experiment. Kronig never appreciated that the SRO theory was correct for both molecules and solids, and the LRO theory was wrong, causing confusion for 40 years. Although in the ensuing years several theorists made the point that the SRO should work for all materials and molecules, since Kronig was so much more prestigious there had to be experimental evidence to support those later claims. This did not occur because both theories could not be calculated quantitatively and the experiments were not reliable. Because no synchrotron sources were available the measurements were tedious and mainly were done

manually over periods of the order of a week per spectrum where stability of the setup was challenging, as was the graduate student's endurance.

To overcome the lack of *quantitative* calculations an elegant experiment was performed by Perel and Deslattes [1] that appeared to have a clever way to distinguish the two theories *qualitatively*. Their idea was to measure the XAFS on a series of perovskites (that have a composition ABO₃) with various A and B atoms. The A and B atoms have different local environments (SRO). They then argued, seemingly correctly, that if the SRO theory is correct the XAFS of all A atoms will be similar and different from those of all the B atoms who would also have similar XAFS among themselves. However, if the LRO theory is valid, then, since the band structure is common to both A and B atoms in a given perovskite they would have similar XAFS but somewhat different ones from the other perovskites which would be expected to have different band structures. They concluded from their measurements that neither theory is supported by their data.

From a historical perspective the question is what went wrong with Perel and Deslattes experiment [1]? We use our new results to address this issue. We find several of the spectra reported in the earlier study are in error, and that the correct spectra for these materials, analyzed in the conceptual context of the earlier study, provide strong support for the short-range model. A more detailed review of the history of the development of XAFS can be found elsewhere.

EXPERIMENTAL

Materials were purchased from Cerac, Inc as powders with nominal size of 200 to 325 mesh. For measurement of the Ca and Ti edges these materials were further refined by suspension in acetone to separate out only grains with diameters of approximately 1 μm or less. The refined powders were mounted on several layers of Kapton tape to provide an effective sample thickness of $\mu\text{x}\sim 1$. Measurements at the Sr and Zr edges were performed on the as-purchased materials, also mounted on Kapton tape with several layers stacked to again provide $\mu\text{x}\sim 1$.

The experiment was performed at the PNC-XOR bending magnet beamline at sector 20 of the Advanced Photon Source at Argonne National Laboratories. A double crystal Si (111) monochromator was used, giving a flux of $\sim 10^{10}$ photons/mm²/sec at the relevant energies. A Rh-coated mirror set at the appropriate cut-off angle was used for harmonic rejection. The incident (I₀) and transmitted (I_T) intensities were measured using ionization chambers. Detector gases were chosen to give approximately 10% absorption in the I₀ detector, and 70% absorption in the I_T detector. At the Ca and Ti edges, N₂ and He were used in both detectors, while at the Sr and Zr edges, N₂ was combined with Ar in the I₀ detector, and Kr in the I_T detector, to give the appropriate absorption values.

RESULTS AND DISCUSSION

Perel and Deslattes [1] measured the Sr, Ti, Zr, and Ca K-edges in SrTiO₃, CaTiO₃, CaZrO₃, and SrZrO₃. In Figure 1 we show their XANES measurements on the Sr, Ti, Zr, and Ca K-edges of SrTiO₃, CaTiO₃, CaZrO₃, and SrZrO₃, and by means of comparison we show in Figure 2 our new measurements on the same materials. The energy axis is scaled with respect to the location of the absorption edge. The discrepancies between the earlier and present study are dramatic for the Zr edges in CaZrO₃ and SrZrO₃ and for the Sr edge in SrZrO₃. It is clear that the experimental unreliability of the data taken in the earlier study is of course, the reason why no conclusion could be made about the correct theory.

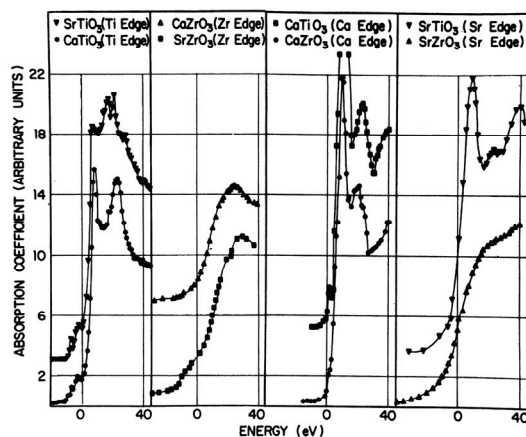


FIGURE 1. The XANES measurements of Perel and Deslattes reproduced from reference [1].

One year after the studies by Perel and Deslattes [1] was reported; Sayers, Stern and Lytle, [5] showed by a Fourier transform (F.T.) that the SRO theory was the correct one for solids, both crystalline and aperiodic cases. Figure 3 and 4 shows the resulting phase shift corrected F.T. that clearly shows the SRO in Ge. This ushered in the modern era of XAFS.

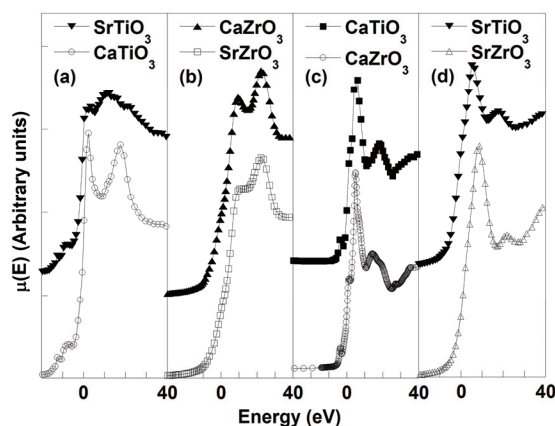


FIGURE 2. Modern XANES measurements of the same materials as in Figure 1. The figure is organized in strict analogy to Figure 1.

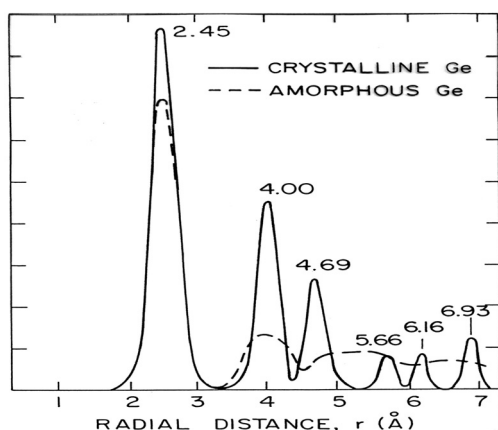


FIGURE 3. Fourier transform (FT) of crystalline and amorphous Ge measured with Lytle's laboratory XAFS facility, reproduced from reference [5].

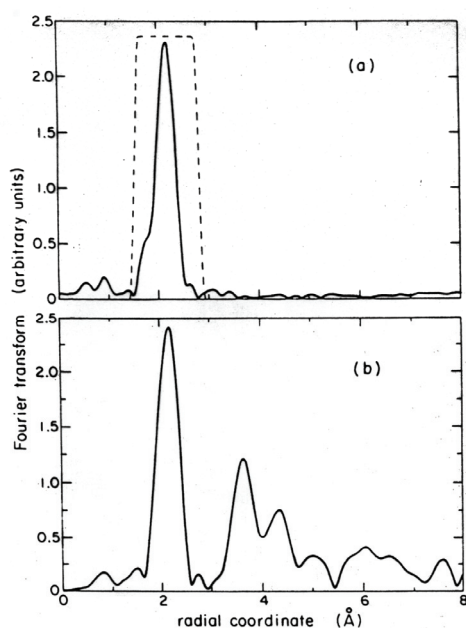


FIGURE 4. Fourier transform of (a) amorphous and (b) crystalline Ge measured later with synchrotron radiation at SSRL. Note that though the data from laboratory facility (Figure 3) had more noise and the resulting F.T. had some spurious features it is clear that only the SRO is being measured, a very robust result.

CONCLUSION

The early years development of XAFS was hampered both by competing theoretical treatments and by the unreliability of many measurements prior to the advent of synchrotron x-ray sources. The introduction of Fourier transforms in XAFS showed directly, robustly, and unequivocally the correctness of the SRO theory without relying on any theoretical analysis, ushering in the modern era of XAFS as a structure determination technique. SRO works for both periodic and aperiodic condensed states while LRO would not cover the aperiodic case. Also, SRO is more efficient for calculation of the XAFS since it depends only on the local structure.

ACKNOWLEDGMENTS

PNC-XOR facilities at the Advanced Photon Source, and research at these facilities, are supported by the US DOE Office of Science Grant No. DEFG03-97ER45628, the University of Washington, a major facilities access grant from NSERC, Simon Fraser University and the Advanced Photon Source. Use of the Advanced Photon Source is also supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38.

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