

BRIEF COMMUNICATION

On the Symmetry of LiCuO₂

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Utsumi *et al.*, *J. Solid State Chem.* **107**, 507, 1993, claim that LiCuO₂ transforms from an orthorhombic modification to a monoclinic one by applying pressure. This interpretation is disputed on the basis of evidence from X-ray and neutron diffraction refinements which show that LiCuO₂ is already monoclinic (NaCuO₂ structure type) at ambient pressure. © 1995 Academic Press, Inc.

This communication comments on "Pressure Effect on the Crystal Structure and Electrical Conductivity of LiCuO₂" by Wataru Utsumi *et al.*, published in *J. Solid State Chem.* **107**, 507 (1993). In their paper the authors claim that the crystal structure transforms as effectuated by pressure. There is evidence that this conclusion is based on weakly founded assumptions.

The basis of their conclusion lies in a combination of new and previously determined diffraction data. The authors published a proposal of the structure of LiCuO₂ that was synthesized for the first time (1). However, the hypothesis (*Cmmm*) was never appropriately supported, and important data were missing in the publication. Only a picture of the proposed structure was given; however, no positional parameters were included, and these will in fact yield unreasonable interatomic distances (2) at variance with EXAFS data (1), which hints that something is in error.

In the pressure experiment, Utsumi *et al.* noted a line splitting that was evident at high pressures and they were able to index the powder pattern, now on a monoclinic cell. From this they concluded that a structural change (of second order) occurred. However, the lack of line splitting is not a proof that the lower symmetry does not prevail over the whole pressure range from the start of the experiment. In fact, there is a smooth change in the values of the lattice parameters that include the virgin sample (their Fig. 5). This could have served as an impetus to reconsider the orthorhombic structure proposal that from many points of view had flaws.

Unaware of the details of the synthesis by Imai *et al.* (1), I synthesized LiCuO₂ following a similar method, using bromine instead of iodine (3). From crystal chemical considerations based mainly on the description of Li₃

Cu₂O₄ (4) as an Li₂CuO₂ · LiCuO₂ intergrowth structure, I successfully refined the cell parameters on a monoclinic cell similar to that of NaCuO₂. Their work then came to my attention but it raised some questions. Upon request, the original powder pattern and refined parameters were kindly put at my disposal (2). According to the powder patterns, the products were most likely identical. An analysis of their powder pattern disclosed that although their model calculates into more diffraction lines (many of which are of zero intensity), it is still incapable of explaining the pattern fully. Most striking is a weak line left over at $d = 1.6 \text{ \AA}$, successfully accounted for by the monoclinic model. In the critiqued paper, this line is unfortunately situated just outside the range of the pressure experiment.

The main structural difference between the orthorhombic and monoclinic models concerns the orientation of the oxygen atoms for which the X-ray data are not too sensitive. The copper atoms which dominate the scattering are practically unaltered, making discrimination between the two models difficult when comparing *R*-factors only. The original structure determination carried its relative "success" from the inability of X rays to discern light elements in a heavy-atom matrix. High temperature factors in their refinement (2) smear out the positions of light atoms to account for the actual error in the model. An X-ray refinement (3) using the monoclinic model gives *as good an R-factor*, explains the entire pattern, and yields reasonable interatomic distances and temperature factors. Moreover, neutron diffraction (3), which better discerns the light elements, clearly showed a preference for the monoclinic model with a Bragg *R*-factor of 3% compared with 13% for the originally suggested orthorhombic model.

Furthermore, the authors claim to have observed *fluorescence peaks* of "included solid iodine." The peaks rather look as if they were due to diffraction. It also seems very farfetched to expect any remaining free iodine when acetonitrile was used as a solvent. On the other hand, remains of solid LiI are also more likely to be found after washing, as is the tetrabutylammonium iodide that was added to the solution, at least according to the first synthe-

sis description (1). Less than 1 wt% iodine was established, and it is unclear to me whether the fluorescence effect would be so strong for such a low content.

In conclusion, the work by Utsumi *et al.* brings interesting data to light concerning the anisotropy in compression and overall temperature dependence of the resistivity of LiCuO_2 . However, their conclusions regarding a structural change upon compression seem doubtful. From X-ray and neutron refinements the NaCuO_2 structure type has been firmly established (3). It is thus more than likely

that the monoclinic symmetry is retained throughout the whole pressure range of the experiment.

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