SHORT COMMUNICATIONS

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Acta Cryst. (1978). B**34**, 1398

Crystal structure of the complex 4,4′,5,5′-tetraethyltetrathiofulvalene–bis(tetracyanoquinodimethane), (TETTF)(TCNQ)$_2$: correction of a printer's error.

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The address given for J. L.. Galigné in the paper by Galigné, Fabre & Giral [*Acta Cryst.* (1977), **B33**, 3827–3831] is incorrect. The correct address is that shown above.

All the relevant information is given in the Abstract.

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Comment on the room-temperature structure of Cs$_2$LiCr(CN)$_6$.

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The room-temperature structure of Cs$_2$LiCr(CN)$_6$ was recently studied by neutron diffraction and reported in the space group *P*4/*mnc* with significant distortion of the Cr(CN)$_6^{3-}$ moiety from O_h symmetry. Both conclusions are inconsistent with earlier Raman, X-ray diffraction, and optical-microscope studies in which the monoclinic space group $P2_1/n$ was assigned. It is shown that Cs$_2$LiCr(CN)$_6$ undergoes two phase transformations above room temperature. The transition at 348 K is first order involving antiferrodisplacive rotation of the Cr(CN)$_6^{3-}$ octahedra ($Fm3m \xrightarrow{348\text{ K}} P4/nmc$). The second-order transformation at 310 K is driven by a soft translational mode condensing out at the zone boundary of the cubic cell ($P4/nmc \xrightarrow{310\text{ K}} P2_1/n$).

The room-temperature structure of Cs$_2$LiCr(CN)$_6$ has recently been studied by profile analysis of neutron powder data (Chowdhury, 1976; Chowdhury, Wedgwood, Chadwick & Wilde, 1977). The reported space group is *P*4/*mnc*. The proposed structure exhibits significant distortions from the high-temperature *Fm*3*m* structure ($T > 348$ K, Ryan & Swanson, 1974) describable in terms of an antiferrodisplacive rotation of the Cr(CN)$_6^{3-}$ octahedron about an axis parallel to the *c* axis and a tetragonal distortion of the octahedron as evidenced by a significant disparity of 0·23 Å in the Cr–C bond lengths. In an earlier publication we reported the results of single-crystal X-ray and vibrational spectroscopic investigation of the same material (Ryan & Swanson, 1976). We feel the correct space group is $P2_1/n$ and find no evidence for distortion of the Cr(CN)$_6^{3-}$ complex ion from O_h symmetry. In addition, we find clear evidence for an antiferrodisplacive shift of the Cs$^+$ ion from its position in the high-temperature *Fm*3*m* structure. The following points support our analysis.

A. Distortion of the Cr(CN)$_6^{3-}$ *ion*

Vibrational spectroscopy provides a very sensitive probe of the departure of a coordination polyhedron from an idealized geometry. There are no detectable splittings of the Cr(CN)$_6^{3-}$ internal modes of vibration in the Raman or IR spectra at room temperature (Swanson & Jones, 1974; Ryan & Swanson, 1976). Furthermore, our refinements of the X-ray intensity data generate Cr–C distances which differ by no more than 0·03 (1) Å.

B. Assignment of the space group

The space group proposed by Chowdhury (1976), *P*4/*mnc*, is inconsistent with the observation of two phase transformations between the *Fm*3*m* phase and the room-temperature phase ($T_c^1 = 348$ K, $T_c^2 = 310$ K). There is no way to generate the high-symmetry *P*4/*nmc* cell given two distinct symmetry changes from the *Fm*3*m* group. The intermediate-phase ($348\text{ K} \geq T \geq 310$ K) space group, which has

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been assigned (Ryan & Swanson, 1976) as *P4/nmc*, derives from a $Cr(CN)_6^{3-}$ rotary mode condensing out at the zone boundary (*X* point). Furthermore, the tetragonal diffraction exhibited by $Cs_2LiCr(CN)_6$ at room temperature is a result of twinning which is clearly evident in the optical properties.

C. Cs^+ *ion translation*

The space group reported by Chowdhury (1976) does not allow translational degrees of freedom for the Cs^+ ion. This is inconsistent with the observation that the second phase change (310 K) is second order involving a soft mode (Raman) which can only be assigned to Cs^+ translational motion (Ryan & Swanson, 1976). Moreover, the X-ray intensities of a class of reflections in $P2_1/n$, which are attributable primarily to Cs^+ displacement, can be traced from below 310 K to zero intensity.

Finally, replacement of the Li atom in the related $Cs_2LiFe(CN)_6$ by Na or K results in room-temperature-stable phases in $P2_1/n$ (Fletcher & Gibb, 1977). The replacement of Li by its larger congeners is roughly equivalent to lowering the temperature of the $Cs_2LiFe(CN)_6$ crystal (Rafalko, Swanson & Beall, 1977). Raman scattering and optical-microscope studies of $Cs_2LiFe(CN)_6$ (Swanson, Lucas & Ryan, 1978) show that this material undergoes two phase transformations below room temperature ($T_c^1 = 221$ K and $T_c^2 = 170$ K). We believe that the temperature-dependent structure of $Cs_2LiCr(CN)_6$ is important in that it is one of a limited set of crystals which exhibit a true second-order structural phase change; heat capacity data for $Cs_2LiCr(CN)_6$ exhibit a small anomaly at 310 K characteristic of a second- or higher-order displacive phase change (McCormack, private communication). It is likely that the lattice instabilities exhibited by $Cs_2LiCr(CN)_6$ are common to several members of the large class of salts possessing the elpasolite structure.

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The room-temperature structure of $Cs_2LiCr(CN)_6$.

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The comments of Ryan & Swanson [*Acta Cryst.* (1978), B**34**, 1398–1399] are acknowledged.

In a previous paper the results were reported of a profile analysis of neutron powder diffraction data on the room-temperature structure of $Cs_2LiCr(CN)_6$ (Chowdhury, Wedgwood, Chadwick & Wilde, 1977). The structure was shown to be consistent with the space group *P4/mnc*. Because of twinning problems it has not been possible to carry out a sufficiently reliable single-crystal analysis of the room-temperature structure of the compound (Ryan & Swanson, 1974); hence the special significance of the powder profile results. According to Ryan & Swanson (1978), the room-temperature structure is $P2_1/n$, there being an intermediate phase transformation between the high temperature ($T > 350$ K) *Fm*3*m* and the room-temperature structure. Their arguments are based largely on the evidence of optical spectroscopic data. In the light of this evidence, the powder data of Chowdhury *et al.* (1977) need to be re-examined; it will then be possible to say whether a better agreement is obtained with the space group $P2_1/n$, proposed by Ryan & Swanson (1978).

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