SHORT COMMUNICATIONS

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Structural phase transformations in dicesium sodium ferricyanide.

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Abstract

A structural phase transformation ($P2_1/n \rightarrow P4/mnc$) has been observed for $Cs_2NaFe(CN)_6$ at 498 K. The structural changes are describable in terms of distortions involving the same phonon modes which are responsible for phase changes in the related $Cs_2LiM(CN)_6$ (M= Cr, Mn, Fe, Co, Ir) salts.

Introduction

In a recent study of structural phase transformations in $Cs_2LiCr(CN)_6$ (Ryan & Swanson, 1976), it was shown that the low-temperature structures ($T < 348$ K) may be characterized by small distortions of the high-temperature elpasoite structure ($Fm3m$) along allowed phonon modes of the $Fm3m$ cell. These conclusions were drawn, in part, from an X-ray diffraction study of a twinned crystal and, while pleasingly consistent with the temperature-dependent Raman spectra, are nevertheless subject to question owing to the lack of suitable single-crystal data (Chowdhury, Wedgwood, Wilde & Chadwick, 1977; Ryan & Swanson, 1978). In particular, it was necessary to assume the space group of the intermediate phase ($310 < T < 350$ K) to be $P4/mnc$ in order to arrive at a reasonable model for the room-temperature $P2_1/n$ phase. Subsequent studies of $Cs_2LiFe(CN)_6$ (Swanson, Lucas & Ryan, 1978) and $Cs_2LiCo(CN)_6$ and $Cs_2LiIr(CN)_6$ (Swanson & Lucas, 1978) have shown that these materials undergo similar phase transformations and that the critical temperatures for the lattice instabilities are related to the size of the Cs^+ ion site in the $Fm3m$ cell. Unfortunately, direct verification of the $P4/mnc$ cell was not possible for any of the $Cs_2LiM(CN)_6$ salts by virtue of twinning problems.

An analogous salt, $Cs_2NaFe(CN)_6$, has recently been studied by single-crystal techniques (Fletcher & Gibb, 1977) and found to crystallize in the space group $P2_1/n$ with cell constants of $a = 7{\cdot}573$, $b = 7{\cdot}709$, $c = 10{\cdot}970$ Å and $\beta = 89{\cdot}994°$. Inspection of the space group, cell size and atomic parameters shows that the room-temperature $Cs_2NaFe(CN)_6$ structure is related to a hypothetical $Fm3m$ structure by the same two phonon modes responsible for the phase transition in the $Cs_2LiM(CN)_6$ salts. The present study was undertaken to determine whether or not $Cs_2NaFe(CN)_6$ exhibits a phase transformation similar to the $Cs_2LiM(CN)_6$ salts and, if so, to observe the critical temperature and the space group of the intermediate phase.

Single crystals were grown by slow evaporation of an aqueous solution of $Cs_2NaFe(CN)_6$, which was obtained from the tripotassium salt *via* cation exchange (Swanson & Ryan, 1973). The optical properties were monitored as a function of temperature (300–600 K) using a Zeiss polarizing microscope and a Mettler FP-3 thermal stage. The diffraction patterns and intensity measurements were made using a Picker FACS-1 diffractometer. Temperature control (±1 K) for the X-ray experiments was effected using a temperature-controlled N_2 flow system with a thermocouple mounted on the goniometer head near the crystal (Smyth, 1972). The crystal was recentered frequently while the temperature dependence of the intensity of the 023 reflection was observed.

The room-temperature structure reported by Fletcher & Gibb (1977) is, no doubt, essentially correct. However, we note that careful inspection of the optical properties of a single crystal shows that no axis of the polarizability tensor is aligned with the monoclinic axis of the crystal, indicating that the symmetry is lower than monoclinic. Also, two reflections (001 and 003), which would be space-group extinct in $P2_1/n$, are detectable on the diffractometer. The stronger of these, 001, diffracts with an intensity which is less than 1·0% of the 004 reflection. In addition, when the cell is indexed on the larger $Fm3m$ cell, the 011 reflection is detectable indicating a doubling of the monoclinic axis along the $\mathbf{a} + \mathbf{b}$ and $\mathbf{a} - \mathbf{b}$ translational directions.

Temperature dependence of the optical properties shows a phase change for $Cs_2NaFe(CN)_6$ at 498 K. No other phase transition was observed in the temperature range probed (to 600 K). The polarizability ellipsoid is uniaxial in the higher temperature phase with the unique axis aligned with the regular parallelepiped morphology of the crystal. The cell constants are found to be $a = b = 7{\cdot}69$, $c = 10{\cdot}97$ Å and $\alpha = \beta = \gamma = 90°$ at 513 K. An X-ray data set collected at this temperature shows extinction conditions consistent with the tetragonal space group $P4/mnc$, in agreement with the previous study of $Cs_2LiCr(CN)_6$. The only violation of this conclusion is the 010 reflection which is detectable with an intensity less than 0·1% of that of the 004 reflection.

Discussion

The present study shows that the $Cs_2NaFe(CN)_6$ material is susceptible to the same lattice instabilities observed earlier for $Cs_2LiM(CN)_6$ salts. Single crystals of $Cs_2NaFe(CN)_6$

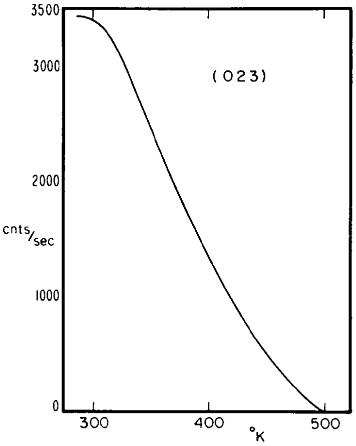

Fig. 1. Intensity of the 023 reflection of $Cs_2NaFe(CN)_6$ as a function of temperature.

can, by virtue of the high critical temperature for the phase II–phase III transition, be obtained in both the tetragonal and monoclinic phases, thereby allowing direct confirmation of the phase II *P*4/*mnc* space group. The cubic to tetragonal phase change observed in the earlier study of $Cs_2LiCr(CN)_6$ is therefore shown, by analogy to the present work, to be an antiferro displacive rotation of the $M(CN)_6^{3-}$ octahedra about the cubic *c* axis as was previously inferred.

Raman spectral data show that the tetragonal → monoclinic phase change in $Cs_2LiM(CN)_6$ salt is 2nd order involving a soft Cs^+ ion translational mode. A plot of the intensity of the 023 reflection for $Cs_2NaFe(CN)_6$ as a function of temperature is shown in Fig. 1. The intensity of this reflection decreases continuously and reversibly to zero intensity at $T_c^2 = 498$ K, as is consistent with a higher-order phase change. Thus, it is likely that the $Cs_2NaFe(CN)_6$ structural change in the vicinity of T_c^2 derives from the same soft Cs^+ translational mode implicated in earlier studies of $Cs_2LiM(CN)_6$ salts. We note, however, that the room-temperature structure of the Na salt (Fletcher & Gibb, 1977) exhibits additional distortions not present in the room-temperature structure of $Cs_2LiCr(CN)_6$. These added distortions from the parent *Fm*3*m* cell correspond to $Fe(CN)_6^{3-}$ rotary and Cs^+ translational symmetry coordinates which also transform as the totally symmetric representation in the $P2_1/n$ cell. Apparently, as the Na crystals are cooled well below T_c^2 the frequency of the soft mode approaches those of other A_1 modes thereby resulting in enhanced mixing and a change in the character of the soft mode.

The critical temperature observed for the Na salt is much higher than those observed for the analogous phase change in the $Cs_2LiM(CN)_6$ salts, as is consistent with the notion that the lattice instabilities result from the Cs^+ ion occupying too large a site in the *Fm*3*m* cell. As the Cs^+ site size increases, the cubic structure becomes less stable thereby driving T_c^1 and T_c^2 to higher temperatures. From the *c* axis length in the tetragonal phase of $Cs_2NaFe(CN)_6$ we estimate a Cs—N nearest neighbor contact distance of *ca* 3·89 Å in the hypothetical *Fm*3*m* phase of the sodium salt. It is striking that in going from $Cs_2LiFe(CN)_6$, where the Cs—N distance is 3·762 Å (Swanson & Ryan, 1973), to the Na salt T_c^2 increases about 330 K.

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References

Chowdhury, M. R., Wedgwood, F. A., Wilde, H. J. & Chadwick, B. M. (1977). *Acta Cryst.* B**33**, 46–51.
Fletcher, R. R. & Gibb, T. C. (1977). *J. Chem. Soc.* pp. 309–316.
Ryan, R. R. & Swanson, B. I. (1976). *Phys. Rev. B*, **13**, 5320–5329.
Ryan, R. R. & Swanson, B. I. (1978). *Acta Cryst.* B**34**, 1398–1399.
Smyth, J. R. (1972). *Am. Mineral.* **57**, 1305.
Swanson, B. I. & Lucas, B. C. (1978). *Inorg. Chem.* **17**, 2717.
Swanson, B. I., Lucas, B. C. & Ryan, R. R. (1978). *J. Chem. Phys.* In the press.
Swanson, B. I. & Ryan, R. R. (1973). *Inorg. Chem.* **12**, 283–286.

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On the existence of low- and high-temperature crystal forms of lithium polyphosphate.

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Abstract

The existence of two crystal forms of lithium polyphosphate $[(LiPO_3)_x.H_2O]$ obtained on crystallization during polymerization of LiH_2PO_4 is confirmed. The different structures occur on growth below or above about 523 K. The transition from the low-temperature to the high-temperature form proceeds very slowly so that differential thermal analysis can only detect it as a very shallow endotherm, peaking at 857 K at a 20 K min^{-1} heating rate. The transition is irreversible and does not occur on cooling. The low-temperature crystal form results from crystallization during polymerization of double PO_4^- tetrahedra to a twisted zigzag chain conformation. Upon annealing, an intramolecular rearrangement