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Thermal Expansion Coefficients of Manganese Fluoride

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The expansivity $(\Delta l/l_{273.2})$ and linear thermal expansion coefficient $[l^{-1}(dl/dT)_p]$ have been measured for the a and c axes of manganese fluoride. There is a marked anomaly in the linear thermal expansion coefficients at the Néel temperature; the Néel temperature was found to be 67°±1°K. The anomaly has the characteristic shape associated with order-disorder transformations.

MANGANESE fluoride has been studied extensively because of the antiferromagnetic transition which occurs at liquid nitrogen temperatures. Many different techniques have been used to measure its properties, e.g., nuclear magnetic resonance,[1] magnetic,[2] and thermal,[3] but in order to utilize these results to the fullest extent, it is necessary to have information about the change in lattice spacing and elastic constants with temperature. The purpose of this paper is to report upon the former, namely the linear thermal expansion coefficients of manganese fluoride.

Manganese fluoride crystallizes in the rutile structure which has tetragonal symmetry and therefore two linear thermal expansion coefficients α_{11} and α_{33} are required to describe the second order strain matrix. [α_{11} refers to the coefficient normal to the c axis (hereafter referred to as α_1) and α_{33} refers to the coefficient parallel to the c axis (hereafter referred to as α_3).] The expansivity, $\beta(\Delta l/l_{273.2})$, was measured by the optical interferometer method and the apparatus has been described elsewhere.[4] The temperature of the interferometer was controlled to within ±0.05°K. The helium 5878 A spectral line was used throughout the investigation to give a resolution of approximately 150 A (i.e., $\frac{1}{20}$ of fringe spacing) for the change in length of the specimens; the specimens where ~6 mm in length.

A single crystal of manganese fluoride was kindly grown by J. M. Nielsen of Bell Telephone Laboratories, Incorporated, for this investigation and two sets of specimens were carefully cut from the crystal with a diamond wheel. One set of specimens was cut with the cone axis parallel to the c axis and the other with it parallel to the a axis. Figure 1 shows the expansivity, β, for the c and a axes as a function of temperature and Fig. 2 shows the linear thermal expansion coefficients α_1 and α_3 as a function of temperature. In each case the reported values of α_1 and α_3 were obtained graphically from a plot of the expansivity with temperature. Table I gives the value of expansivity β and linear thermal expansion coefficients, $l^{-1}(dl/dT)_p$ for both a and c axes, between 10°K–280°K.

From Fig. 1 it can be seen that there is a marked change in the slope at the Néel temperature, T_N, which was found to be 67°K±1°K; this results in the typical order-disorder transition type of curve for α_1, and α_3. It is immediately obvious that the a axis does not show such a large variation in expansivity as does the c axis but at 170°K the a axis starts to increase in length with decreasing temperature giving rise to the negative values of α_1 below this temperature. This expansion of

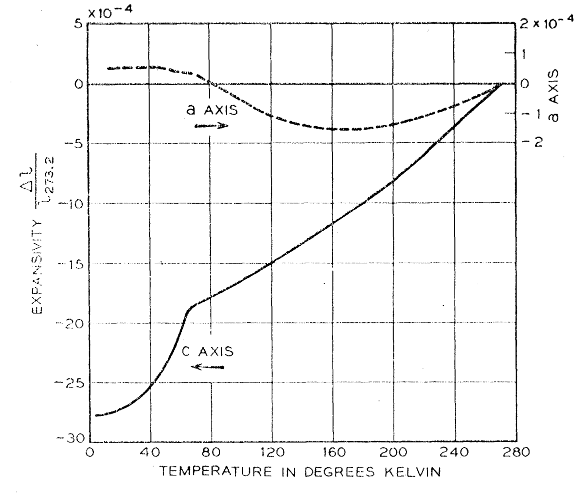

FIG. 1. The expansivity $(\Delta l/l_{273.2})$ of manganese fluoride along the c and a axes.

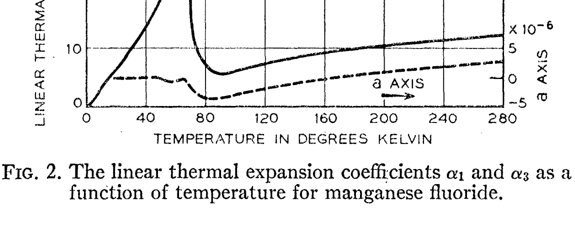

FIG. 2. The linear thermal expansion coefficients α_1 and α_3 as a function of temperature for manganese fluoride.

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[1] R. G. Shulman and V. Jaccarino, Phys. Rev. **108**, 1219 (1957).
[2] M. Griffel and J. W. Stout, J. Chem. Phys. **18**, 1455 (1950).
[3] J. W. Stout and H. E. Adams, J. Am. Chem. Soc. **64**, 1535 (1942).
[4] D. F. Gibbons, Phys. Rev. **112**, 136 (1958).

the *a* axis may be the result of short-range order occurring above the Néel temperature. However, since the expansivity along the *a* axis is an order of magnitude less than that along the *c* axis the total volume of the crystal continues to decrease. In Fig. 1 it can be seen that approximately $\frac{1}{3}$ of the total change in length between 280°–0°K occurs below T_N, and is the result of the antiferromagnetic ordering. The total change in length between 0°–273.2°K is $\sim 0.3\%$ along the *c* axis which is unusually large for an essentially ionic lattice (of the crystalline solids the metals have large expansivities and of these aluminum has one of the largest, 0.38% in the same temperature range) and gives an indication of the relatively large energy associated with the antiferromagnetic ordering. Foex[5] has measured the variation of linear thermal expansion coefficient with temperature for a series of antiferromagnetic oxides and finds a similar well-defined λ-type transition. The oxides have cubic symmetry, however, and so numerical comparisons would not be meaningful.

Qualitatively it is possible to interpret these results in terms of the antiferromagnetic exchange energy arising from an interaction through the *p* orbitals of the fluorine atoms. The greater the decrease in the *c* spacing the greater will be the overlap between the manganese *d* states and the fluorine *p* states thus increasing the exchange interaction. However, if the *a* axis continued to expand, it would in effect decrease the exchange interaction by increasing the $\mathrm{Mn}\uparrow$–$\mathrm{Mn}\downarrow$ spacing. Thus, below the Néel temperature, although the *c* axis is decreasing rapidly (Fig. 1), the *a* axis spacing remains constant below 50°K.

To calculate the energy associated with the antiferromagnetic ordering from these results and compare it with that obtained from thermal measurements it is necessary to know the change in compressibility with temperature. The elastic constants are being measured so that such a comparison can be made.

TABLE I. Expansivity and linear coefficient of thermal expansion.[a]

T(°K)	$\beta=\Delta l/l_{273.2}$		$\alpha=l^{-1}(dl)/(dT)_p$	
	$\beta_1\times10^4$	$\beta_3\times10^4$	α_1 (10^{-6} °K^{-1})	α_3 (10^{-6} °K^{-1})
10	+0.51	−27.70	...	...
15	+0.51	−27.62	...	+3.25
20	+0.51	−27.37	...	+6.40
30	+0.51	−26.51	...	+10.33
40	+0.51	−25.31	...	+13.85
50	+0.45	−23.72	−0.99	+18.35
60	+0.36	−21.49	−0.55	+26.29
70	+0.31	−18.55	−1.46	+13.34
80	+0.06	−17.70	−3.46	+6.59
90	−0.28	−17.13	−3.20	+5.34
100	−0.59	−16.52	−2.84	+6.36
110	−0.85	−15.84	−2.40	+6.97
120	−1.07	−15.10	−1.93	+7.45
130	−1.24	−14.33	−1.56	+7.86
140	−1.37	−13.54	−1.17	+8.23
150	−1.45	−12.74	−0.76	+8.57
160	−1.52	−11.92	−0.40	+8.92
170	−1.54	−11.03	+0.06	+9.22
180	−1.52	−10.10	+0.39	+9.54
190	−1.45	−9.12	+0.70	+9.83
200	−1.37	−8.05	+0.97	+10.11
210	−1.25	−7.07	+1.21	+10.38
220	−1.13	−6.03	+1.48	+10.67
230	−0.97	−4.97	+1.71	+10.93
240	−0.79	−3.87	+1.94	+11.15
250	−0.59	−2.74	+2.22	+11.47
260	−0.35	−1.58	+2.50	+11.73
270	−0.09	−1.21	+2.78	+12.02
280	+0.20	+0.81	+3.02	+12.23
65				+43.43
67				+55.83

[a] Subscript 1 refers to the *a* axis and subscript 3 to the *c* axis.

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[5] M. Foex, Compt. rend. **227**, 193 (1948).