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Light Scattering Study of the Phase Transitions in Some Improper Ferroelectrics and Ferroelastics

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Raman scattering is used for the study of the soft modes behaviour near the phase transitions occuring with the doubling of the unit cell. Improper ferroelectrics and ferroelastics $Gd_2(MoO_4)_3$ and $Tb_2(MoO_4)_3$, pure ferroelastic $KFe(MoO_4)_2$ and ferroelectric TSCC are studied. The acoustic phonons and elastic constants in these crystals are investigated by Brillouin scattering method.

Three examples of our recent light scattering works illustrate the behaviour of ferroelectrics and ferroelastics with improper type phase transitions.

§1. Rare Earth Molybdates

$Gd_2(MoO_4)_3$-GMO and $Tb_2(MoO_4)_3$-TMO crystals are isostructural and can be considered as classical examples of improper ferroelectrics. Theoretical[1,2] and neutron scattering studies on TMO[3] have established that the transition is a cell doubling one and is accompanied by the instability of the doubly degenerate zone boundary optical mode. So, below the phase transition two A_1 soft modes should appear in Raman spectra. One of them was observed by Fleury[4] in GMO. The search for the second soft mode for a long time was unsuccessful. At last at 77 K near the soft A_1-mode one more mode was found (in Raman[5] and IR[6] spectra) suggestively attributed to a second soft mode. It was impossible to follow its temperature variation due to strong broadening and overlaping of the modes already at room temperature, i.e. far below $T_c = 433$ K. Takagi *et al.*[7] made an attempt to calculate the contour of this complicated line and came to a conclusion about anticrossing of the two soft A_1-modes.

Our results[8] show that the Raman tensor for A_1-mode, which was observed by Fleury[4], is highly anisotropic. In YY-polarization this mode is not observed at all, but another low frequency A_1-mode is well seen (Fig. 1). Within the accuracy of the experiment the temperature behaviour of the $A_1(LO)$ and $A_1(TO)$ components of both soft modes is the same. This result differs from[5] where the softening of the $A_1(LO)$-mode was not observed.

In Raman spectra we detected a broad central component intensity of which increases when approaching T_c from below. Two low frequency Raman spectra at room temperature and near T_c are given in Fig. 2. Far from T_c ($T = 295$ K) one of the soft modes is seen, while the central component is nearly absent, the peak at the centre being the light scattering from longitudinal acoustic phonons. With a narrow spectral slit Brillouin components can be resolved (Fig. 2, in the middle). Near T_c the soft mode becomes overdamped and a broad central component appears (Fig. 2, upper part). The intensity of the central component increases strongly near T_c and drops abruptly below T_c. The central

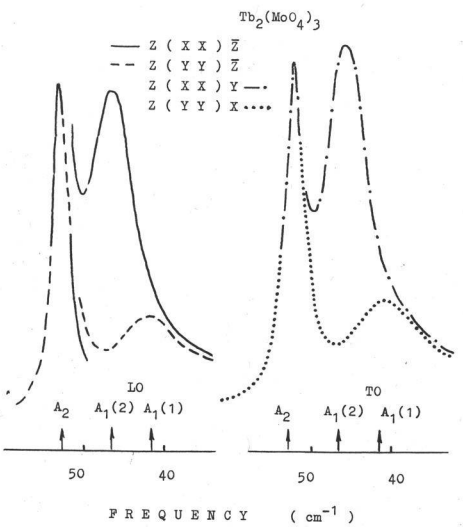

Fig. 1. Low frequency $A_1(LO)$ and $A_1(TO)$ Raman spectra of TMO for different polarizations at 295 K.

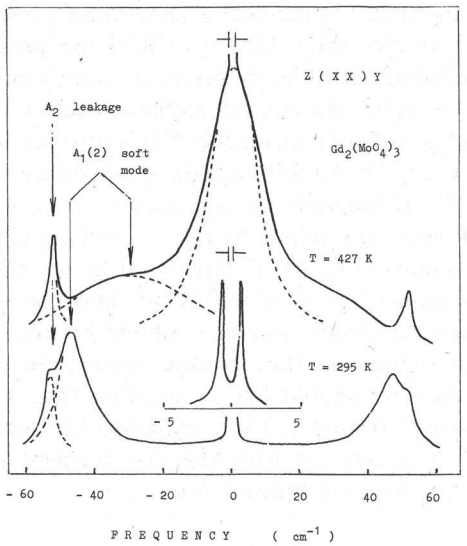

Fig. 2. $Z(XX)Y$ spectra of the diffusive central mode far and close to T_c in GMO.

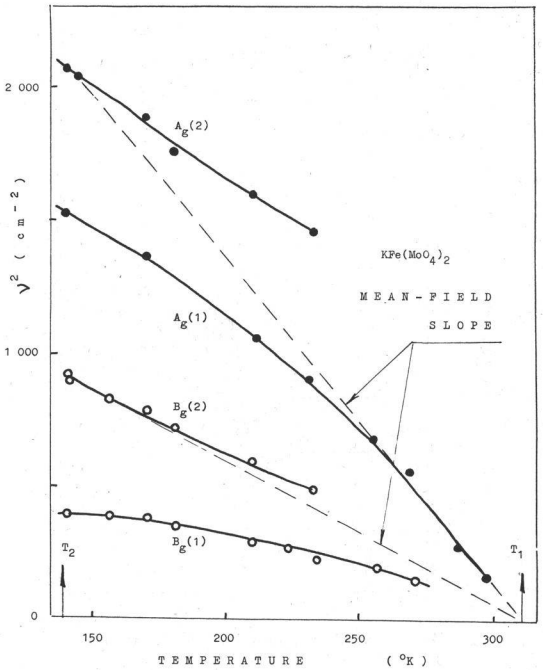

Fig. 3. Temperature dependence of the square of A_g and B_g modes frequency in $KFe(MoO_4)_2$.

component halfwidth decreases when approaching T_c from 50 cm^{-1} at $T_c - T = 80°$ till 15 cm^{-1} at $T_c - T = 15$ K.

§2. Trigonal Molybdates

As it is shown by different studies[10-12] $KFe(MoO_4)_2$-KFM crystals undergo at $T_1 = 312$ K a continuous ferroelastic transition from a trigonal symmetry (space group D_{3d}^3)[13] to a monoclinic symmetry (point group C_{2h}). We revealed another phase transition at $T_2 = 139$ K, which is found to be of the first order.[11]

The transition to the ferroelastic phase is manifested by considerable changes in Raman spectra, namely, by the appearance of new modes and by splitting of E_g-modes. The behaviour of the low frequency part of the spectra appears to be most interesting. In the paraelastic phase no phonon modes are observed in this part of the spectra (0–50 cm^{-1}), whereas in the ferroelastic phase 4 modes ($2A_g + 2B_g$) appear. At least 2 modes $A_g(1)$ and $B_g(1)$ behave as soft modes, their frequency goes to zero when the temperature approaches T_1 from below. The temperature dependence of the square of the frequency of the soft and hard modes is plotted in Fig. 3. Dashed lines in Fig. 3 show the mean-field slope. Departures from mean-field theory seem to occur due to the soft modes-hard modes coupling.

Brillouin scattering measurements have been performed above and below T_1. Elastic constants of KFM were calculated from the observed Brillouin shifts (Fig. 4). In the monoclinic phase a c_{44} anomaly occurs on a 40 degrees temperature range. The addition of the six order terms to the expression of the free energy allows a correct description of the experimental results for this elastic constant. In trigonal phase anomalous variations of c_{12}^0, c_{44}^0 and c_{66}^0 appear near T_1. These results can be understood as arising from the fluctuations of the order parameter and anharmonic coupling between the soft mode and the acoustic mode.

§3. The Ferroelectric Phase Transition in TSCC

The ferroelectric phase transition from nonpolar into polar orthorhombic phase in trissarcosine calcium chloride (TSCC) is known long ago[14] and results of investigations show that TSCC is a uniaxial ferroelectric with a second order phase transition of the order-disorder type[15-18].

An intense mode with characteristic features of a soft mode appears in the Raman spectra below T_c.[19] It is found that this polarized mode has the $A_1(Y)$ symmetry, Y being the polar axis.

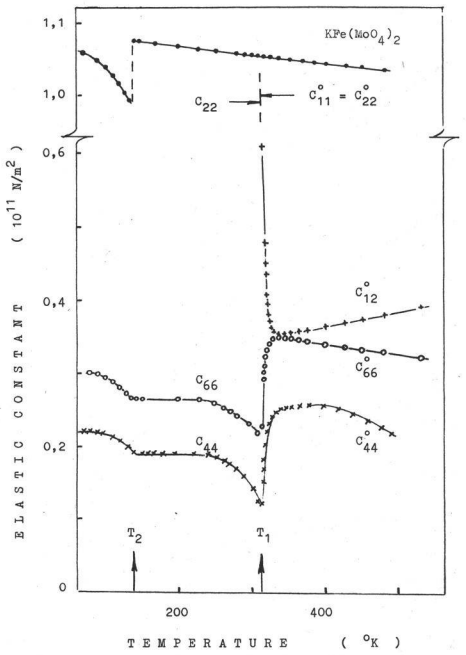

Fig. 4. Tgmperature dependence of elastic constants in $KFe(MoO_4)_2$.

When approaching T_c from below the frequency of $A_1(TO)$ mode becomes very low and we could follow it from 28 to 10 cm^{-1} in the interval $0{,}6 \leqslant T/T_c \leqslant 0{,}85$, in which the soft mode frequency varies as $(T_c - T)^{0{,}42}$. We compared the $A_1(TO)$- and $A_1(LO)$-modes behaviour when approaching T_c from below and found that it is identical in general features. So, our results show that in TSCC the phonon contribution to the dielectric constant's anomaly is small and can not explain such a strong increase of ε_y which reaches 600 according to the last data.[18] We followed the temperature variation of longitudinal and transverse acoustic phonons determined by c_{11}, c_{22} and c_{44} elastic constants (Fig. 5). A large step in c_{22} elastic constant $\Delta c_{22} = 2{,}5 \cdot 10^9$ N/m^2 may be produced by electrostrictive coupling between the soft mode and the acoustic branch. In conclusion we should like to mention that if the phase transition in TSCC is really of the order-disorder type, at least the displacement processes play a significant role.

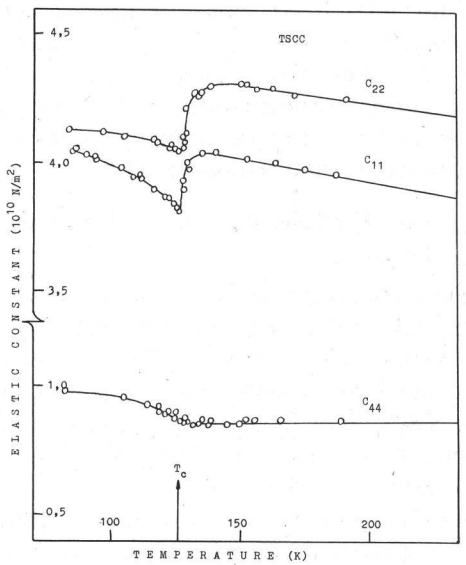

Fig. 5. Temperature dependence of elastic constants in TSCC.

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