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LETTER TO THE EDITOR

Indications of a ferroelastic phase transition in $CaMoO_4$ from pulsed electron paramagnetic resonance and dielectric studies

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Abstract. Measurements of the electron spin–lattice relaxation time T_1 of a paramagnetic hole centre in x-irradiated $CaMoO_4$ are presented. The temperature dependence of T_1 indicates the interaction of the hole centre with an acoustical branch and an optical branch with B_g symmetry via Raman processes. The spin–lattice relaxation time T_1 shows a striking anomaly at 52 K, typical of a second-order phase transition. We explain the T_1-behaviour in terms of a softening of the optical phonon branch. At the same temperature, anomalies of the phase memory time T_M and the dielectric permittivity were also observed. It is concluded that $CaMoO_4$ undergoes a second-order ferroelastic phase transition at $T_C = 52$ K.

Calcium molybdate belongs to the group of crystals with the so-called scheelite structure. They are characterized by the $I4_1/a$ space group with two ABO_4 molecules (A = Ca, Bi, La, Sr, ...; B = W, Mo, V, Nb, ...) per primitive unit cell. It is known that the isostructural crystals $BiVO_4$ and $LaNbO_4$ exhibit a ferroelastic phase transition at $T_C = 528$ K and 768 K, respectively [2, 4]. The space group changes from $I4_1/a$ to $I2/a$. The phase transition is related to a soft optical phonon with B_g symmetry coupled with an acoustical B_g mode. The aim of this work is to show by means of electron spin-relaxation studies and dielectric measurements that a similar structural phase transition takes place also in calcium molybdate.

A hole centre created by x-irradiation at 77 K and used as a paramagnetic probe shows anomalies in its EPR spectra and relaxation at low temperatures [6]. The centre structure is such that one electron is removed, leaving a hole in one of the nonbonding p orbitals of the oxygen ligands of the MoO_4^{2-} complex. This centre is stable at temperatures below 150 K.

The crystals studied were grown by the Czochalski method. After x-irradiation at a temperature of 77 K the sample was put into a Oxford CF935 or ESR910 cryostat. The electron spin-relaxation measurements were carried out on a BRUKER ESP 380 FT-EPR spectrometer and on a home-built pulsed EPR spectrometer, both working at X-band frequencies. The spin–lattice relaxation time T_1 was measured by the inversion–recovery method using a π–T–$\pi/2$–τ–π–τ–echo sequence or by signal saturation of the primary echo sequence by changing the repetition rate of the echoes: $\pi/2$–τ–π–τ–echo–T–$\pi/2$–τ–π–τ–echo–T– $\cdots$. The phase memory time T_M was extracted from the decay of the amplitude of the conventional two-pulse echo. The pulse widths used on the BRUKER and on the home-built spectrometer were $t_p^{\pi/2} = 96$ ns and $t_p^{\pi} = 192$ ns.

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The dielectric measurements were performed on an HP2484A capacitance bridge. The sample used was a gold-plated single crystal with 96 mm^2 area and 1.9 mm thickness where the applied electric ac field was oriented along the *c*-axis.

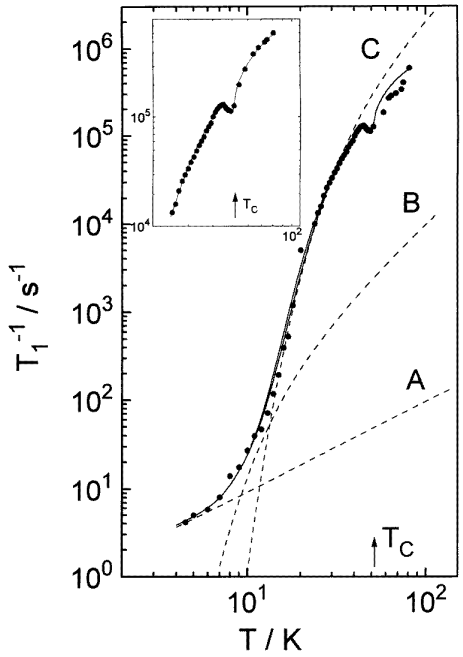

Figure 1. The temperature dependence of the spin–lattice relaxation rate T_1^{-1}. The full points show the experimental data. The solid line shows the fit with equations (1), (2), (3) and (4). The dashed lines marked with A, B and C show the contributions of the first, second and third terms of equation (1). The inset shows the relaxation rate measured at around T_C with higher accuracy and the fit with equations (1), (2), (3) and (4).

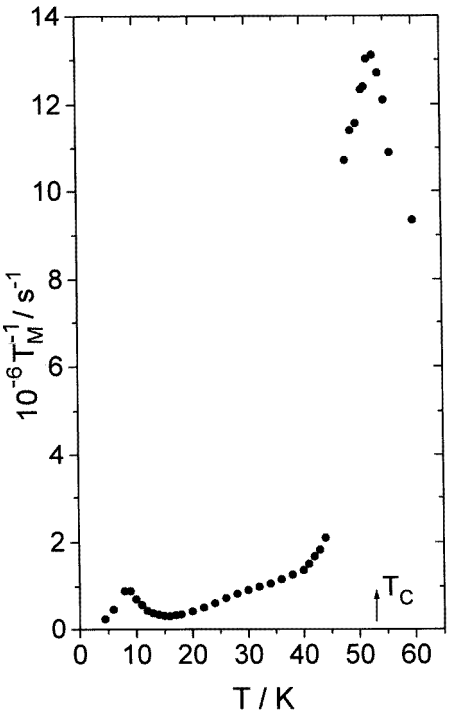

Figure 2. The temperature dependence of the transversal relaxation rate T_M^{-1}.

The measured temperature dependence of the spin–lattice relaxation rate T_1^{-1} of the hole centre in $CaMoO_4$ is presented in figure 1. It can be described by the formula [1]

$$T_1^{-1}(T) = AT + C_8 T^9 \frac{I_8(\theta/T)}{I_8(\infty)} + \frac{1}{4} B \operatorname{cosech}^2\left(\frac{T_B}{2T}\right) \tag{1}$$

with the transport integral

$$I_8(\theta/T) = \frac{1}{8\pi^9} \int_0^{k\theta/h} \omega^2 \operatorname{cosech}^2\left(\frac{\hbar\omega}{2kT}\right) \mathrm{d}\omega \tag{2}$$

where the first two terms are the contributions of an acoustic phonon branch with a Debye temperature θ via direct and Raman processes. The third term is characteristic of Raman processes with an optical phonon branch. A fit of the experimental data provides the parameters $A = 0.96\ s^{-1}\ K^{-1}$; $C_8 = 2950\ s^{-1}\ K^{-9}$; $\theta = 53$ K; $B = 58.5 \times 10^6\ s^{-1}$ and $T_B = 155$ K. The value of θ should not be expected to coincide with the Debye temperature of

the crystal measured with thermodynamic methods because θ is related to only one of the acoustical phonon branches. A comparison with data from optical Raman scattering [3] shows that there is a good agreement of the optical mode energy kT_B corresponding to 108 cm^{-1} measured in this work with the wave number of the longitudinal optical B_g mode of 110 cm^{-1} determined by the optical spectroscopy. That is why we conclude that the relaxation rate T_1^{-1} at temperatures $T > 20$ K is primarily determined by this external optical mode with B_g symmetry.

We observe an anomalous reduction of the relaxation rate in a temperature range around $T = 52$ K. Such an anomalous temperature behaviour of the spin–lattice relaxation rate is known to be typical of crystals with a second-order structural phase transition [5]. An analytical description of the spin–lattice relaxation anomaly is possible taking into account the influence of a critical mode damping in the third term of equation (1) in the form

$$B = B' \frac{5}{\pi} \int_0^1 \mathrm{d}x \int_0^1 \mathrm{d}x' \; \frac{x^2 x'^2 / 2\Gamma}{((x - x')/2\Gamma)^2 + 1} \tag{3}$$

with $B' = 5.85 \times 10^6$ s^{-1} and using for the mode damping an empirical expression:

$$\Gamma(T) = \frac{1}{2}|T - T_C|^{-0.5} + \frac{1}{16\,000} T^2 + 0.05 \tag{4}$$

with $T_C = 52$ K. The inset in figure 1 shows the fit of T_1^{-1} with equations (1), (2), (3) and (4).

Figure 2 shows the experimental values of the transversal relaxation rate T_M^{-1}. Also, in T_M^{-1} we observe a critical anomaly at $T_C = 52$ K correlated with the anomaly in the longitudinal relaxation time T_1. We can interpret this critical increase of the transversal relaxation rate as the contribution of the elastic order parameter fluctuations near the structural phase transition.

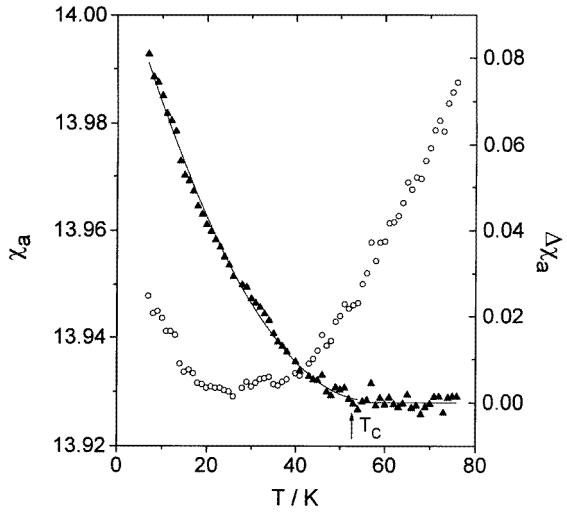

Figure 3. The temperature dependence of the dielectric susceptibility of a gold-plated $CaMoO_4$ crystal with the applied ac field in the *c*-direction. The open circles show the measured dielectric susceptibility values χ_a. The triangles represent the deviation $\Delta\chi_a$ of the measured dielectric susceptibility from the linear extrapolation of the high-temperature susceptibility above T_C.

The results of dielectric measurements are shown in figure 3. The temperature dependence of the dielectric permittivity at temperatures above $T_C = 52$ K is caused by the linear thermal expansion of the crystal. Below this temperature the dielectric behaviour changes. There is an additional contribution to the electric susceptibility increasing with decreasing temperature. We relate this contribution to a second-order ferroelastic phase transition in $CaMoO_4$. The Landau theory for a ferroelastic phase transition of second order with the elastic order parameter η coupled to the electric degrees of freedom gives a free energy of

$$F = F_0 + \frac{1}{2}\alpha(T - T_C)\eta^2 + \frac{1}{4}\beta\eta^4 + \frac{1}{2}a\eta^2 E_a^2 + \frac{1}{2}b\eta^4 E_a^2 + \frac{1}{2}\chi_a^0 E_a^2. \qquad (5)$$

The parameters a, b, α, β are expansion coefficients, χ_a^0 is the static electric susceptibility and E_a is the applied electric field. This leads to a temperature-independent contribution to the electric susceptibility $\chi_a = \chi_a^0$ at temperatures $T > T_C$ and a temperature-dependent part

$$\chi_a = \chi_a^0 + (a\alpha/\beta)(T - T_C) + (\alpha^2 b/\beta^2)(T - T_C)^2 \qquad \text{for } T < T_C$$

which qualitatively explains the observed experimental behaviour of $\Delta\chi_a$ near the phase transition temperature with the parameters $a\alpha/\beta = 1.916\,99 \times 10^{-4}$ K^{-1} and $\alpha^2 b/\beta^2 = 3.240\,46 \times 10^{-5}$ K^{-2}.

The results shown lead us to the conclusion that $CaMoO_4$ undergoes a ferroelastic phase transition of second order at $T_C = 52$ K analogous to that in the isostructural scheelite compounds $BiVO_4$ and $LaNbO_4$.

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