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Abstract
The magnetic phase transition 3 mL' .tautm. m with the Curie temp. Tc .simeq. 30K was studied by optical domain anal. and birefringence measurements using polarized light microscopy. The domain structure is consistent with .hivin.43mL'Fm with 24 partially ferromagnetic/fully ferroelec./fully ferroelastic orientation states. The weakly ferromagnetic m phase possesses a spontaneous magnetization perpendicular to the (110)cub planes (mirror m). A coupling effect between the ferromagnetic, ferroelec. and ferroelastic domains was obsd. and detected. The spontaneous birefringence of magnetic and possibly coupled structural origin vanishes above Tc and exhibits a 2nd order character of transition.

Reference

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OPTICAL DOMAIN, FERROIC COUPLING AND BIREFRINGENCE STUDIES OF THE MAGNETIC PHASE TRANSITION IN Fe-I BORACITE

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ABSTRACT: The magnetic phase transition $3m1' \leftrightarrow m$ with the Curie temperature $T_C = 30K$ has been studied by means of optical domain analysis and birefringence measurements using polarized light microscopy. The domain structure is consistent with the species $43m1'Fm$ with 24 partially ferromagnetic /fully ferroelectric / fully ferroelastic orientation states. The weakly ferromagnetic m phase possesses a spontaneous magnetization perpendicular to the $(110)_{cub}$ planes (mirror m). A coupling effect between the ferromagnetic, ferroelectric and ferroelastic domains was observed and detected. The spontaneous birefringence of magnetic and possibly coupled structural origin vanishes above $T_C$ and exhibits a second order character of transition.

Key Words: magnetic phase transition; domains; birefringence; ferroic coupling; Fe-I boracite.

1. INTRODUCTION

Single crystals of members of the boracite family continue to remain attractive thanks to their ferroelectric, ferroelastic and ferromagnetic properties. The Fe-I boracite ($Fe_3B_7O_{13}$) exhibits a sequence of structural phase transitions from the cubic prototype $43m1'$ to the orthorhombic $mm21'$, the monoclinic $m1'$ and the trigonal $3m1'$ phases, as was established by optical domain, X-ray and Mössbauer studies. This sequence comprises all the non-magnetic phases disclosed up to now in the boracites except for the tetragonal $42m1'$ phase, uniquely present in Cr-Cl. At low temperature an essentially antiferromagnetic order appears below the Curie temperature $T_C = 30 K$ with a weak ferromagnetic moment revealed by magnetic hysteresis loops. By analogy with the Co-Cl boracite, which shows the same phase sequence as Fe-I and a magnetic phase with symmetry m below $T_C = 10 K$, the magnetic symmetry of Fe-I would be expected to be m, too. With a view to finding more detailed information about the magnetic phase transition and the related magnetic group, the phase transitions at low temperature in Fe-I crystals have been studied in the present work by means of optical domain observations and birefringence measurements with the help of polarized light microscopy (PLM).

2. EXPERIMENTAL

Single crystals of Fe-I boracite were grown by the chemical vapour transport technique. Platelets were cut parallel to $(100)_{cub}$, $(110)_{cub}$ and $(111)_{cub}$ and electroded by deposition of semi-transparent Au-Cr layers, which permit both a simultaneous optical control of the domain states during poling and birefringence measurements perpendicular to the sections. Samples were mounted on a rotating rod in an optical He-flow cryostat, specially adapted to a polarized light microscope. The birefringence was measured both with a tilting compensator and with a system combining a photoelastic modulator, a Babinet-Soleil compensator, a
rotatable polarizing microscope, a micro-photometer and a "lock in" amplifier. The spontaneous charges and currents were detected by using an electrometer.

3. RESULTS AND DISCUSSIONS

3.1 Electric Field Poling of the 3m1' Phase

The symmetry of the ferromagnetic low temperature phase, supposed to be m, requires the spontaneous magnetization vector $\mathbf{M}_s$ to be perpendicular to the mirror, whereas the spontaneous polarization vector $\mathbf{P}_s$ may adopt an arbitrary direction within the mirror plane. However, due to the second order character of the magnetic phase transition (see item 3.4) the neighbouring phase 3m1' imposes $\mathbf{P}_s$ to be along $<111>$ at the Curie temperature and, depending on the strength and character of the magneto-structural coupling, it may rotate more or less off that direction in the mirror plane of the monoclinic phase upon decreasing temperature.

Because the species 43m1'F3m1' of Fe-I permits 4 fully ferroelectric/fully ferroelastic domain states with the spontaneous polarization $\mathbf{P}_s$ along the four polar axes // $<111>$, as schematically shown in Fig. 1(a) on a (111) plane, poling of the 3m1' phase was carried out at first. Since the $<111>$ directions of the mother phase 43m1' are already polar (owing to the boron-oxygen net), the 180° domain switching of $\mathbf{P}_s$ is impossible in the 3m1' phase. However, reorientation of domains ("jumping") is permitted between these four preferential directions. Therefore poling with an electric field $\mathbf{E} // <111>$ can give rise to a monodomain with $\mathbf{P}_s$ perpendicular to the (111) plane, as observed in Fig. 1(b). After reversal of the field polarity, the single domain splits up into a maximum of three possible domain states with the $\mathbf{P}_s$ and optical axis directions forming an angle of $\arctan \sqrt{2}/2$ with the (111) surface. The extinction of the three domains are related by a rotation of 120° (60°), thus contrast between the three domains was observed in Figure 1(c) at a suitable intermediate position of the crossed Nicols. The single domain in Fig. 1(b) appeared black between crossed polarizers, i.e. optically isotropic with the spontaneous polarization and thereby the optical axis perpendicular to the crystal plane, consistent with the trigonal symmetry.

This switching process was carried out near 165 K just after the m1' $\rightarrow$ 3m1' transition. A field strength of 100 kV.cm$^{-1}$ was found to be necessary to switch the polarization on a (111) plane of 20 μm thickness. This poling field increased rapidly with decreasing temperature. Very high switching field strengths were also found in other trigonal boracites. Some birefringent traces subsisted even when increasing the field strength up to 150 kV.cm$^{-1}$. They are due to domains with inclined $\mathbf{P}_s$ which could be blocked by some defects in the crystal or by some polishing scratches. Other trigonal boracites such as Fe-Cl also showed this phenomenon.

It should be noted that the application of an electric field ($\mathbf{E} // <111>$) in the mm21' or m1' phases gave rise to some domains which subsisted metastably in the low temperature phases and prevented the 3m1' phase to be poled completely with $\mathbf{P}_s // \mathbf{E}$. It seems that the field along $<111>$ would have "enforced" some states in the mm21' or m1' phases, which can only be suppressed by heating up to the cubic phase.

3.2 Magnetic Phase Transition 3m1' $\leftrightarrow$ m

Once established, the poled single domain state on (111) remained stable without back-switching of domains to other orientations, even after removal of the poling field at 40 K. Upon further cooling below the Curie temperature $T_C=30$ K, it split up into weakly birefringent, hence ferroelastic domains. Under the action of a magnetic field, these domains...
can be switched, and accordingly their extinction and birefringence reoriented, indicating that they actually result from the magnetic ordering below $T_C$. Figure 2 (a, b) shows this domain pattern.

The Faraday effect, which is responsible for the visibility of the ferromagnetic domains in the case of Co-Cl boracite at low temperature, does not seem to be the cause of the observed domains in Fe-I, since no contrast of circular birefringence, due to the left and right hand rotation of light with a component "up" or "down" of the spontaneous magnetization $M_s$, could be observed, neither by inclining the platelet, nor by uncrossing slightly the polarizers. This observation suggests that the birefringent domains generated in the magnetic phase must result from a magneto-structural coupling and a symmetry reduction owing to the magnetic ordering below $T_C$, and thus be ferroelastic. Three domain orientations can be discerned in Figure 2 by turning the microscope around its axis. The extinctions of the domains were determined by means of a micro-photometer because of the weak contrast. The indicatrix sections were found to be related by rotation of 60° (or 120°), with the larger index $n_y$ parallel to $<110>_{cub}$ crystal edges. This domain structure is consistent with the symmetry m for the weakly ferromagnetic phase below $T_C$.

In fact, the corresponding monoclinic m deformation necessarily provokes a tilting of the optical indicatrix which becomes at the same time optically biaxial on going through the transition at $T_C$, as shown in Figure 3. Therefore, birefringent domains with the indicatrix section ($n_x$, $-n_y$) can be observed on the initially optically isotropic (111)${}_{cub}$-section. Since a (111)${}_{cub}$ cut through a 3m1' single domain includes three equivalent (110)${}_{cub}$ mirror planes, three types of domain may be generated, all birefringent and mutually related by rotations of 120° (or 60°), as illustrated in Fig. 2(c). The fact that the indicatrix section so formed possessed the smaller index $n_x$ parallel to $<112>$${}_{cub}$ and the larger one $n_y$ parallel to $<110>$${}_{cub}$ on (111)${}_{cub}$, indicates that the initial optical indicatrix is uniaxially negative, as is also the case for other trigonal boracites.

As concerns the magnetic domain orientation, the symmetry m allows a non-zero spontaneous magnetization $M_s$ perpendicular to the (110)${}_{cub}$ plane (mirror m). Each ferroelastic domain permits two ferromagnetic domains with opposite axial vectors $M_s$, parallel to the $n_y$ axis (see Fig. 2(b)). These antiparallel ("180°") magnetic domains were not visible under PLM owing to the absence of a sufficiently strong Faraday effect. It should be noted that the birefringent domains resulting from the magnetic phase transition can only be observed when starting from a poled 3m1' single domain state on (111)${}_{cub}$, because of the weak contribution of the magneto-structural deformation to the birefringence, which would be "immersed" in the strong background birefringence of the domains of other orientations.

3.3. Coupling Between Ferroic States

The fact that the optical domains switched under the action of a variable magnetic field with observable exchange of birefringent contrast, implies a coupling between the ferromagnetic and ferroelastic states. Attempts were made to measure the spontaneous charges or currents during the magnetic domain switching. Figure 4(a) shows that in the weakly ferromagnetic m phase, by applying externally a permanent magnet (≈ 400 Oe) and by varying its direction, sharp pulses of spontaneous current ($I_{max} \approx 10^{-4}$ A.m$^{-2}$) with fluctuating sign were detected. Optical visualization showed that the current peaks were in fact related to the switching of the ferroelastic domains. The spontaneous charge density presented also sharp peaks with an order of magnitude of $10^{-5}$ C.m$^{-2}$ (Fig.4(c)). Above the Curie temperature $T_C$, however, neither current nor charge signals can be measured, as shown in Fig. 4(b, d).

In the m phase the magnetic domain reorientation by 60° (or 120°) commanded by a variable magnetic field, leads via magneto-structural coupling to the switching of the
Figure 1. (a) Schematic of the 4 fully ferroelectric / fully ferroelastic domain states of the species 43m1'F3m1', presented on a (111)cub cut of Fe-1; (b) Isotropic monodomain state of the 3m1' phase with $P_S$ and optic axis (O.A.) perpendicular to the (111)cub plane (20 μm thick), observed after poling (E=100 kV.cm⁻¹) at one polarity. (c) Three remaining possible domain states of the 3m1' phase with the $P_S$ and O.A. inclined by ≈ 35° to the (111)cub surface, obtained after reversal of E.

Figure 2. Ferroelastic domain structure split from a 3m1' single domain with $P_S \perp (111)cub$ surface (Fig.1b) owing to the ordering of the weakly ferromagnetic m phase: (a) Observed domain pattern (T=15 K); (b) Domain state after switching from (a) by the action of a variable magnetic field; (c) Schematic drawing showing the three ferroelectric/ferroelastic domains and the antiparallel magnetizations of the ferromagnetic 180°-domains inside the ferroelastic domains.

Figure 3. Schematic explanation of the optical indicatrix rotation due to the magneto-structural transition from 3m1' (a) to m (b), giving rise to the domain structure shown in Fig. 2c.
ferroelastic domains among the three possible orientations on an initially poled trigonal single domain. Owing to the ferroelectric/ferroelastic coupling, this switching necessarily results in the jumping (pivoting) of the spontaneous polarization $P_s$ between the three equivalent states around the original polar axis direction of the 3m' phase. During these switchings, the part of $P_s$ due to a magneto-strictive contribution could be expected to decay and be reestablished, giving rise to the alternating weak charge or current pulses.

3.4. Birefringence Measurements

Figure 5 gives the temperature dependence of the spontaneous birefringence $\Delta n_s$ in one of the magnetically split ferroelastic domains on (111)$_{cub}$ between 10 and 40 K. $\Delta n_s$ decreased progressively upon heating and vanished at the Curie temperature $T_C=31$ K, where simultaneous optical control indicated the disappearance of domains, proving readily the magneto-structural origin of the birefringence. The birefringence shows a small value of 2.7x10^{-4} at 10 K ($\lambda=542$ nm). An anomalous dip in the slope of the $\Delta n_s(T)$ curve, reproducible upon various measuring runs, can be observed, although no change in domain structure was visible by the naked eye. This behaviour may be attributed to a change of magnetic ordering as in the case of Cr-Cl boracite or to a Schottky-type anomaly as found in Co-boracites. The variation of $\Delta n_s(T)$ in the monoclinic m phase results both from the thermal rotation and uniaxial $\Rightarrow$ biaxial deformation of the optical indicatrix.

4. CONCLUSIONS

The optical domain studies on Fe-I boracite by means of PLM, in conjunction with birefringence and electric measurements allow us to draw some conclusions:

1). The magnetic ordering at the Curie temperature $T_C=30$ K gives rise to a weakly ferromagnetic phase of symmetry m, with the spontaneous magnetization $M_s$ perpendicular to the (110)$_{cub}$ planes (mirror m). The related magneto-structural deformation 3m' $\Rightarrow$ m results in the splitting-up of a trigonal monodomain with $P_s$ perpendicular to the (111)$_{cub}$ into three ferroelectric/ferroelastic domains with weak birefringence or into 2x3 states when including the 180°-ferromagnetic sub-domains. The domain structure agrees with Aizu species 43m'Fm which allows 12x2 partially ferromagnetic/fully ferroelastic/fully ferroelastic orientation states.

2). If we consider a 3m' single domain as the prototype, which was in fact the experimental situation of our sample after electric poling along <111>$_{cub}$, the m phase of the species 3m'Fm is now fully ferromagnetic, i.e. all ferromagnetic domains have different orientations of $M_s$ and all ferroelastic ones may be commanded by a magnetic field.

However, if we take 43m' as the prototype, the m phase of the species 43m'Fm becomes "partially ferromagnetic", which means that at least one additional ferromagnetic domain orientation exists in which the $M_s$ vector has the same orientation as in the first, but with differently oriented spontaneous deformation (i.e. in a different ferroelastic domain). This situation arises when the specimen is not poled in the trigonal state.

The results from the qualitative experiments of domain switching demonstrate well the existence of a coupling effect between the ferromagnetic, ferroelectric and ferroelastic domain states. The coupling between the ferroelastic and ferroelectric domains is full in the sense that there exists an entire coupling between $P_s$ and the spontaneous deformation. The coupling between the ferromagnetic and ferroelastic or ferroelectric domains, however, is partial due to the axial property of $M_s$.

3). The temperature variation of the spontaneous birefringence clearly indicates the magnetic origin of the ferroelastic domains and a 2nd order character of the magnetic 3m' $\leftrightarrow$ m phase transition, as is consistent with most of the magnetic transitions. The
magnetic ordering usually gives rise to a rather weak magnetostrictive distortion of the crystal lattice, not strong enough to provoke a first order transition.

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