Letters

The Growth of Large Single Crystals of Lithium Ferrite

The growth is reported of single crystals of lithium ferrite with dimensions sufficient for the production of magnetoelastic delay-line specimens. Preliminary measurements have been made of some magnetic and microwave properties of the crystal.

It is well known that the magnetic and elastic properties of lithium ferrite lead one to expect that this material would find ready application in the field of magnetoacoustic delay lines and magnetoelastic parametric amplification. However, such application has been prevented to-date by the lack of lithium ferrite single crystals of the required dimensions. The present communication reports an attempt to produce a single crystal suitable for this purpose.

The composition of the melt was as follows:

	Li_2CO_3	Fe_2O_3	B_2O_3	PbO
(mole % wt)	12.31	23.09	20.28	44.32

The melt was heated to 1060° C in a 500 ml platinum crucible for a period of 12 h, and a negative temperature gradient of 0.7° C/cm was maintained over the height of the crucible during this period. The temperature was then reduced at 0.8° C/h to 600° C, when the furnace was switched off. The resulting lithium ferrite crystals consisted of six specimens of approximately 1 cm side, and one specimen, shown in fig. 1, with a side of 2 cm and of weight 36 g. Gamma-radiographs of this latter crystal showed regions, clear of flux inclusions, which are large enough to cut out rods suitable for acoustic resonance experiments. However, the gamma-radiographs, together with X-radiographs, showed the existence of striae which are parallel to the growth interface and which may be associated with either the occurrence of constitutional supercooling or fluctuations in the temperature control during the cooling cycle. Also, the appearance of the larger crystal is consistent with the existence of parallel growth. The smaller crystals showed crystal faces which were more nearly perfect but with the basic structure seen in the photograph.

Atomic absorption spectrum analysis has shown that the iron-to-lithium ratio of the crystals corresponds to a chemical formula: $Li_{0.45}Fe_{2.52}O_4$.

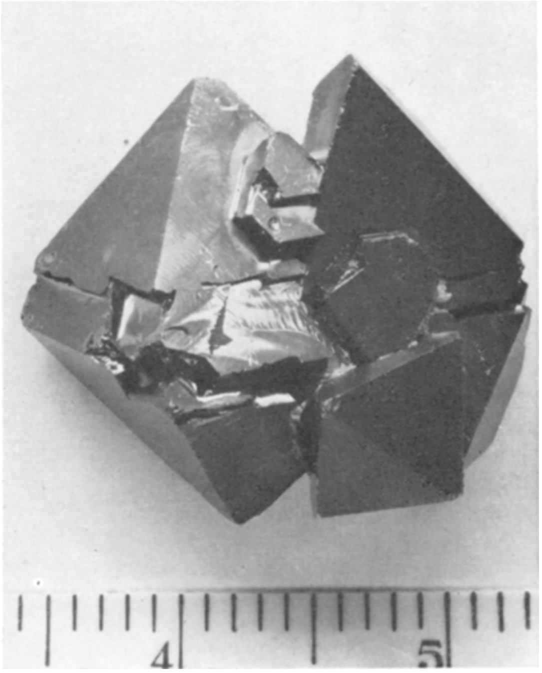

Figure 1 (1.0 in. = 25.4 mm)

The initial measurements carried out on the crystal yielded the following results:

Resistivity	25000 Ω cm
Curie temperature	635.5° C
Saturation magnetisation (0° K)	4052 G
Magnetic moment per molecule (0° K)	2.519 μB
g-factor (300° K)	2.071
$2K/M$ (300° K)	−558 Oe
ΔH (300° K) (as prepared from melt)	15 Oe
ΔH (300° K) (quenched after 4 h annealing at 750° C)	7 Oe

The increase in linewidth over the value of 1.8 Oe, reported by Remeika and Comstock [1], and the values of the resistivity and the magnetic moment may be due to the excess of iron in the crystal giving rise to Fe^{2+} ions.

Acknowledgements

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Reference

1. J. P. REMEIKA and R. J. COMSTOCK, *J. Appl. Phys.* **35** (1964) 3320.

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Hydrothermal Synthesis of Iron Molybdates

The crystal structures of the transition metal molybdates and tungstates are of interest because the structures of these complex oxides reveal a surprisingly large number of changes going along the series increasing the number of 3d or 4f electrons. The marked changes in volume per formula weight found in going from one member of the series to another also suggests that there might be interesting and correlated changes in the structure of a single species at different pressures. The crystal structures of some of the transition metal molybdates have been studied by Abrahams [1] and others [2]. A study of trivalent molybdates [3] has shown that $Fe_2(MoO_4)_3$ is isomorphous with scandium molybdate, which has the same orthorhombic structure as scandium tungstate [4]. However, Pliasova *et al* [5] have reported that $Fe_2(MoO_4)_3$, when crystallised hydrothermally [6], has a monoclinic structure. It was therefore of interest to investigate whether $Fe_2(MoO_4)_3$ can exist in different, pressure-dependent polymorphs.

The dry oxides Fe_2O_3 and MoO_3 were mixed together in the molar ratios of 1:3 and sealed into platinum capsules with a solution of $FeCl_3$. Two sizes of platinum capsule were used, with internal capacities of $\frac{3}{4}$ and $\frac{1}{5}$ cm^3. The charges of solid oxides were 50 and 30 mg respectively. Solutions of $FeCl_3$ which were 5 and 12 wt % both gave the same results. The platinum capsules were pressurised and heated in a standard "Tem-Pres" hydrothermal apparatus for periods between 4 to 12 days, and then quenched and opened.

It was found that, at pressures below about 400 bars (1 bar = 750 torr), the product was $Fe_2(MoO_4)_3$. After 4 days at 460° C, the crystals were only a few tenths of a millimetre in size, and the product contained unreacted Fe_2O_3 and MoO_3. After 12 days at 475 to 485° C, the reaction was complete. Single crystals of $Fe_2(MoO_4)_3$ grew as greenish-yellow, thick plates up to 1 mm in size. These monoclinic crystals were examined by X-ray diffraction using a precession camera, and the lattice constants were found to be [7]

$$\begin{aligned} a &= 15.55 \pm 0.05\ \text{Å} \\ b &= 9.27 \pm 0.04\ \text{Å} \\ c &= 18.08 \pm 0.07\ \text{Å} \\ \beta &= 124.8 \pm 0.2^\circ \end{aligned}$$

These are in good agreement with those determined by Pliasova, which were

$$\begin{aligned} a &= 15.52\ \text{Å} \\ b &= 9.21\ \text{Å} \\ c &= 18.10\ \text{Å} \\ \beta &= 125^\circ \end{aligned}$$

In the absence of good single-crystal measurements for orthorhombic $Fe_2(MoO_4)_3$, it is not possible to determine with certainty which form has the smaller volume per unit formula weight. Approximate calculations from powder patterns suggest that the X-ray density of the orthorhombic form is slightly the smaller, and so it might be expected to form at the lower pressures. The lowest pressure investigated was 170 bars and, at this pressure, the product was still monoclinic $Fe_2(MoO_4)_3$. The transition point between the monoclinic and orthorhombic polymorphs must therefore lie between 170 bars and ambient pressure.

At pressures greater than about 650 bars, the same reactants, at 480° C, produced deep-blue acicular crystals up to a few millimetres in length, but very thin. The crystals commonly grew as rosettes of radiating clusters, and the reaction appeared to be complete within 4 days. This product was identified as the high-pressure form of $FeMoO_4$, having the wolframite structure [7]. It is interesting to note that Young and Schwartz [8] synthesised this compound in powder form by heating FeO and MoO_3 together at 900° C and 60 kbars; whereas, in this work, it has been produced hydrothermally as