AN X-RAY METHOD FOR DEFINING COMPOSITION OF A MAGNESIUM SPINEL[1]

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The three refractory magnesium spinels ($MgAl_2O_4$, $MgCr_2O_4$ and $MgFe_2O_4$) form a complete series of solid solutions at high temperature.
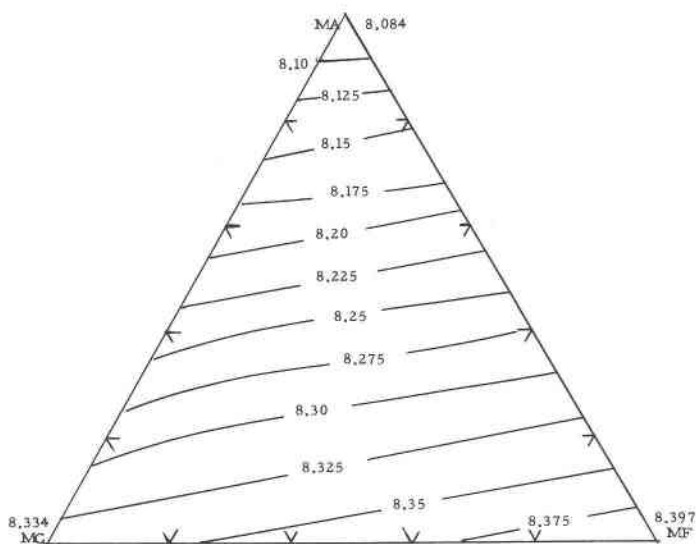

FIG. 1. Lattice parameters in the system $MgAl_2O_4$—$MgCr_2O_4$—$MgFe_2O_4$—(quenched from 1600° C.). Abbreviations are MA, MC and MF, respectively.

At temperatures below 1000° C., there is exsolution in the binary $MgAl_2O_4$-$MgFe_2O_4$. The relationships in this system have been presented by the author elsewhere (Allen, 1964).

Detailed study shows significant deviations from Vegard's law in two of the three bounding binary systems, but on a gross scale the ternary system shows nearly a planar variation of lattice parameter with molar composition (Fig. 1). Similarly, index of refraction (Fig. 2) and density,

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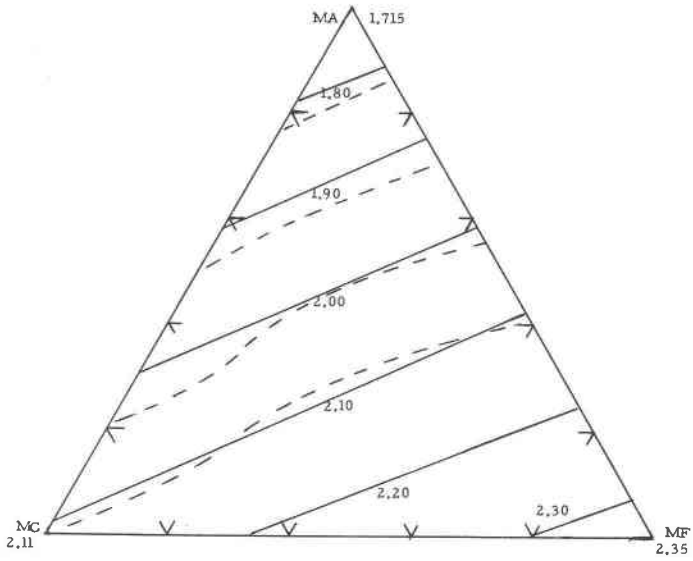
FIG. 2. Refractive index of homogeneous spinel in the System $MgAl_2O_4$—$MgCr_2O_4$
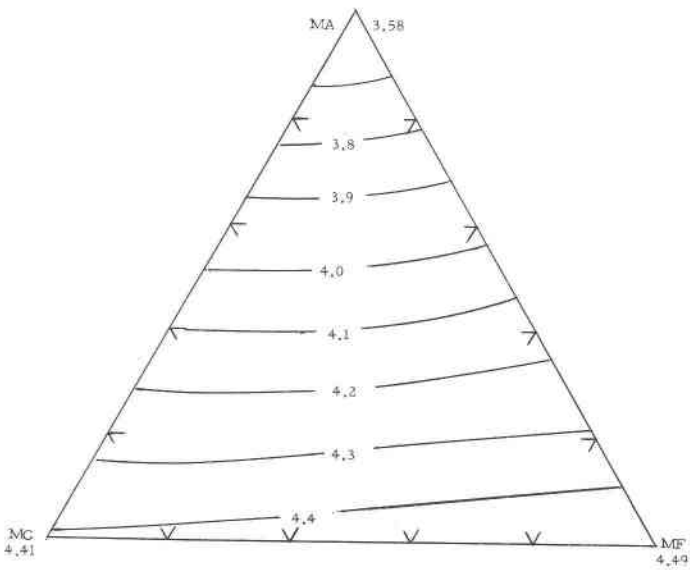—$MgFe_2O_4$. Solid line—calculated, dashed line—observed.

FIG. 3. Calculated density in the system $MgAl_2O_4$—$MgCr_2O_4$—$MgFe_2O_4$
(quenced from 1600° C.).

as calculated from the cell size (Fig. 3), show similar patterns of variation. Since lines of equal value for all three parameters trend in approximately the same direction, it is impossible to fix the composition of a mixed spinel by measuring any two of these parameters.

Diffractograms of the three end members show wide variation in the relative peak heights of the (111), (220), (400), (422) and other peaks (Table I). This suggests that an intensity parameter might be correlated with composition of the solid solution. Since the entire ternary diagram was covered at 10 mol % intervals in the course of this research, and

TABLE I. RELATIVE PEAK HEIGHTS OF Mg SPINELS[1]

	hkl	$MgAl_2O_4$	$MgCr_2O_4$	$MgFe_2O$[2]
	111	35	67	7
	220	39	13	33
	311	100	100	100
	222	4	10	3
	400	57	52	27
	331	—	5	—
	422	10	4	11
	511, 333	47	32	30
	440	62	44	41
Ratio	220/111	1.1	0.2	4.7
Ratio	400/422	5.7	13.0	2.45
	Lattice	8.0843	8.3340	8.397
	Parameter a.u., ±	0.0012	0.0010	0.005

[1] Averages of several diffractograms; not corrected for peak width.

[2] Quenched from 1000° C. or above; below that temperature, the cell size decreases.

x-ray patterns[3] were made of each composition, abundant data were available.

The ratios of the peak heights of various pairs of peaks were plotted on the ternary diagram; among them were the ratios

$$\frac{I(111)}{I(311)}, \frac{I(220)}{I(311)}, \frac{I(220)}{I(111)}, \text{ and } \frac{I(400)}{I(422)}.$$

With many compositions, different samples or even different patterns on the same sample would yield different values for the ratio selected. By averaging several values for each composition, plots were obtained in

[3] Norelco diffractometer; Ni-filtered Cu radiation, fed through pulse height analyzer set for maximum peak-to-background ratio; scanned at 1° 2θ per min. (or $\frac{1}{4}$° for some runs); cell sizes calculated from (844), (931) and (951) peaks.

which the lines of equal intensity ratio were approximately perpendicular to the lines of Figs. 1, 2 and 3.

The ratio

$$\frac{I(220)}{I(111)}$$

was finally selected since it was the most reproducible from pattern to pattern, and since the point values progressed in the most orderly man-
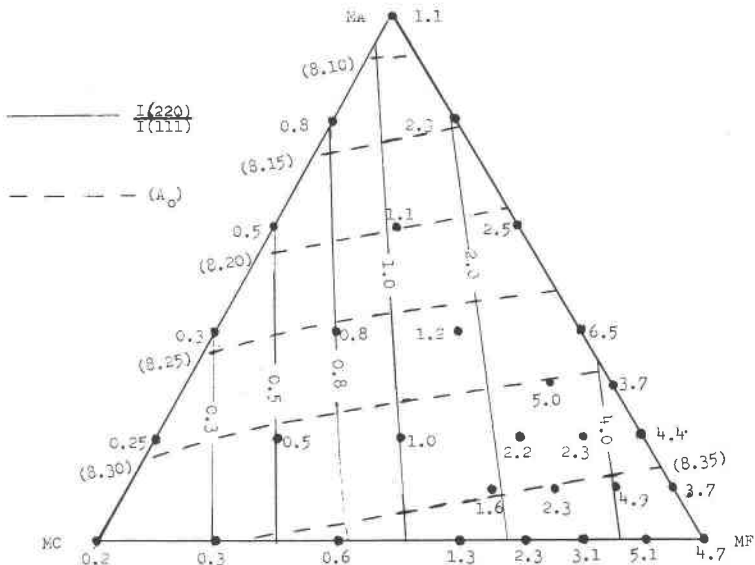

Fig. 4. Lines of equal ratio $\dfrac{I(220)}{I(111)}$ in the system

MgAl$_2$O$_4$—MgCr$_2$O$_4$—MgFe$_2$O$_4$ (high-temperature form only).

ner. Figure 4 shows the plot of this particular ratio. Lines of equal cell size are also shown by dashed lines.

Therefore a single x-ray diffraction pattern will yield two easily calculated parameters—the cell size and the ratio of two peak heights—which can be plotted on a grid of intersecting coordinates to yield the composition of the spinel. The values of Fig. 4 are not claimed to be absolute, but probably vary with different equipment. However, a chart can be prepared for any facility if a range of compositions is available.

These results apply only to solid solutions of these three magnesium spinels. They would not directly apply where significant amounts of

Fe^{2+}, Zn, Mn, Ni, Co, or other divalent ions are present, but there is no reason why a similar type of result might not be found in other systems. An example of a system in which this method may prove useful is the steelmaker's high-fired chrome-periclase refractory, in which the resulting spinel after service is essentially a complex Mg spinel; any original FeO has been oxidized and combined with free MgO to form additional "$MgFe_2O_4$" molecule.

REFERENCE

ALLEN W. C. (1964) Solid solution in the refractory magnesium spinels. Ph.D. thesis, Rutgers—The State University, New Brunswick, N. J.

THE ORIGIN OF MECHANICAL TWINNING IN GALENA

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In the course of a general investigation into the plastic properties of galena (Lyall and Paterson, 1965) it was found that mechanical twinning with composition plane (441) could be produced in single crystals tested in compression at room temperature and at 2.5 and 5 kilobars confining pressure, provided the crystals had an initial length to cross-section area ratio less than 0.7 and were oriented so that the resolved shear stress on {001} ⟨110⟩ slip systems was initially zero; otherwise {001} ⟨110⟩ slip occurred. Both the general appearance and annealing behavior of these experimentally produced twins are quite distinct from that of (441) lamellar twins which occur in large single crystal blocks of galena from Broken Hill, New South Wales. The latter (Fig. 1a) are commonly 10 to 50 μ thick, discontinuous and never intersect; they anneal by blunting (Cahn, 1954) and absorption by the parent crystal (Fig. 1b). The experimentally produced twins (Fig. 1c) are invariably thicker by an order of magnitude or more, form highly strained junctions and anneal by recrystallization and grain growth within the twin volume (Fig. 1d).

Consideration of the effects of high temperature and high pressure on mechanical twinning in minerals (Cahn, 1954) and the effects of shock loading and high strain rates on mechanical twinning in metals (Rinehart and Pearson, 1954; Zukas and Fowler, 1961) suggested that the (441) lamellar twins in the Broken Hill crystals might have been pro-

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