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Reflection of X-rays from the (100) Face of Fluorite

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X-ray spectral lines, (200) weak, (400) strong, and (600), reflected from the (100) face of fluorite were obtained by the photographic method using wave lengths from approximately 1100 to 3000 X.u. In each case the intensity of the (200) reflection was compared, by visual estimation, with the intensity of reflection of the Cu $K\alpha_1$ line. Since many of the elements producing the lines were not themselves suitable for use as targets, the radiation was obtained by rubbing the element, or some of its compounds in powder form, on a copper target. Because the powder is gradually driven from the target under the electron bombardment, the observed intensities of the (200) reflections so produced are somewhat lower than those which would have been obtained if the entire target had consisted of the solid element. It was found that the (200) reflection was much greater in the region 1300 to 3000 X.u. than for shorter wave lengths.

Introduction

As in all face-centered cubes, the (100) reflection from fluorite is totally absent, and the (200) reflections are also nearly null, because, parallel to the layers of Ca atoms, and half way between them are F atom layers containing nearly the same number of electrons as the calcium layers. Considering the ions of Ca and F to be point sources, we should have, for the intensity ratio (200)/(400), approximately $(20-18)^2$: $(20+18)^2 = 1/361$.

Experimental method

The (200) reflections of fluorite have generally been considered to be absent, or at best, very faint (Pealing (1921), James & Randall (1926), MacInnes & Shedlovsky (1926) and Havighurst (1926)). MacInnes & Shedlovsky (1926) found the ratio of the intensity of the (200) spectrum to that of the (400) to be about 1/100, while Pealing (1921) found it to be about 1/800. Since Havighurst (1926) used the powder method the Ca–2 F reflectoins fell so near other stronger ones due to Ca alone that it was difficult to distinguish them directly. By properly combining reflections, however, he calculated Ca–2 F values which agree rather well with ours. The investigations to which the above references are made were all carried out with $K\alpha$ radiation from the heavier elements Mo (42) and Pd (46). The corresponding wave lengths are 707 and 584 X.u. respectively. As far as we are aware there has been no attempt to obtain the (200) reflections at longer wave lengths. We first tried the Cu $K\alpha$ lines from a copper target, and when the (200) intensity appeared to be about 3% that of the (400) we proceeded to other wave lengths in this region.

The photographs were all made with a Siegbahn vacuum spectrometer of 18 cm. radius. It was provided with a single crystal and a single slit of width 0·1 mm. The only material in the path of the beam between target and photographic film was two very thin pieces of aluminum foil, one near the slit and the other between the crystal and the photographic film. These foils served to shield the film from visible light from the filament and from scattered radiation. To check the absorption caused by the aluminum foils the upper (or lower) half of the photographic film was covered by the foil, and it was found that for wave lengths below that of Rh $L\alpha_1$ ($\lambda = 4588$) one layer of the foil did not cause enough absorption to be detected by the eye. Hence the variation in absorption of aluminum with wave length was neglected.

Two crystals were used, both from the Mahoning mine, Rosaclaire, Ill. On each crystal there was a region of about 2×3 cm. in which the (100) face was good enough to give a rather sharp reflection of an object, such as the edge of a window. The three films reproduced in the paper show fairly good lines. Since the quantity in question is only the ratio of reflecting powers, (200)/(400), imperfections in the crystal faces are likely to affect both terms of the ratio in nearly the same way. About four fifths of the films were taken with one of the crystals which was the clearer of the two and seemed to have somewhat the better face. There was no certain difference in the results obtained by the two, hence the two groups were not kept separate. The faces were not treated in any way except to clean them with alcohol, but were used just as they were obtained from Mr Earl W. Martin, Ann Arbor, Mich.

The (200) reflections were run from 10 to 60 times as long as the (400) which were usually one minute runs, in order to obtain comparable blackening on the film. The two lines to be compared were taken on the same film about $\frac{1}{2}$ cm. apart and the ratio of their intensities was estimated visually. After correcting for time of exposure, as explained immediately preceding Table 1, the ratio was taken to be the ratio of the (200)/(400) reflections.

The voltage on the primary of the power transformer was always kept at the same value, constant to about 5%, for both the (200) and the (400) reflections taken on the same film. The supply voltage was the 110 volt power line, which ordinarily varies by only a few volts. The resistance of the transformer primary circuit was at the same setting for both orders of reflection. The primary voltage was kept constant by adjusting the filament current of the X-ray tube. In this way we consider that the power supplied to the X-ray tube was constant to a degree better than the accuracy of estimation of relative intensities of the spectral lines.

The (200) reflection was obtained for the $K\alpha_1$ lines of all the elements from Se (34) to Sc (21) inclusive, except As (33). The edge of the unit cell of fluorite is 5450 X.u. Therefore wave lengths greater than 2725 X.u. cannot be obtained in the (400) reflection, and it was thought best to take Cu $K\alpha_1$ (400) as a constant reference line. Since the Ta $L\alpha_1$ line has nearly the same wave length as the Cu $K\alpha_1$ a check was made, using the Ta $L\alpha_1$ from a tantalum target in both the (200) and the (400) reflections. The result agrees satisfactorily with the $K\alpha_1$ lines. One observation was also made of the (600)/(400) ratio for the Cu $K\alpha_1$ line. The (200) reflections, for all except copper and tantalum, were taken by rubbing a generous coating of the metallic element, or one of its compounds, on the anode of copper, while the (400) standard reflections were taken from the copper anode. The radiation from a solid target of the element concerned would surely be stronger than that from the powder used, hence the proper value for the (200) reflection would be somewhat greater than that observed. This is important to note, considering the much fainter (200) reflections reported previously. A comparison of results (not included in Table 1) of the reflection from a solid iron target with the results obtained from iron oxide on the copper target showed that the solid iron target gave (200) lines which were noticeably stronger. Two voltages were used on the X-ray tube; approximately 30 kV. peak and 22 kV. peak. Tests showed that no certain difference could be observed in the intensities of the Cu $K\alpha$ line at the two voltages. This was because the electrical connections were such that the tube current varied nearly inversely as the primary voltage when the filament current was changed.

The accompanying Figures, 1(*a*), (*b*), and (*c*) are samples of both (200) and (400) reflections of $K\alpha_1$ lines. The (400) is that of Cu $K\alpha_1$ in all three cases, while the (200) reflections are of three different elements as explained in the description below the Figures.

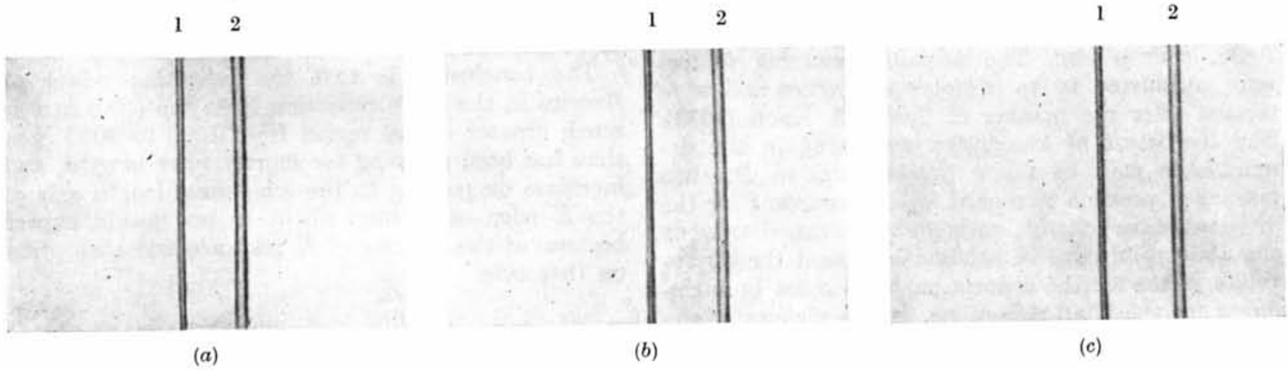
Observations and results

As an illustration of how the ratio of the observed intensity (200)/(400) was obtained, consider a film on which the (200) reflection came from Fe_2O_3 rubbed

Table 1. *Fluorite* (200) *reflections of the* $K\alpha_1$ *lines of* 13 *elements compared with the* (400) *reflections of* Cu $K\alpha_1$

The last two lines are: (*a*) the (200) reflection of Ta $L\alpha_1$ compared with (400) of the same line; (*b*) Cu $K\alpha_1$ (600) compared with Cu $K\alpha_1$ (400).

X.u.	Element	Relative intensity × 10^3 obs.	$\frac{\varrho(200)}{\varrho(400)} \times 10^3$ calc.
1103	Se (34)	3·2	11·9
1251	Ge (32)	3·3	13·3
1337	Ga (31)	16	14·1
1432	Zn (30)	14	15·2
1537	Cu (29)	28	16·7
1655	Ni (28)	42	18·4
1785	Co (27)	38	20·1
1932	Fe (26)	30	23·2
2098	Mn (25)	47	26·7
2285	Cr (24)	40	31·8
2498	V (23)	48	40·0
2743	Ti (22)	43	55·8
3025	Sc (21)	51	141
3060	K absorption edge of calcium		
1519	Ta (73)	22 (*a*)	16·4
1537	Cu (29)	38 (*b*)	26·1



(*a*) (*b*) (*c*)

Fig. 1. Spectra of three different elements. (200) reflection of (*a*), zinc; (*b*), cobalt; (*c*), manganese. (1) is the $K\alpha$ doublet of these elements; (2) is the Cu $K\alpha$ doublet in the (400) reflection

on a copper target. The ratio of the blackening of Fe $K\alpha_1$ (200) to Cu $K\alpha_1$ (400) was estimated to be 4/3. The (200) reflection was exposed for 35 min. and the (400) for one min. Therefore the observed ratio of intensities is $4/(3\times 35) = 0{\cdot}038$. Table 1 gives a list of the emission lines of 13 elements in the (200) reflection, all $K\alpha_1$ lines, compared with the reference line Cu $K\alpha_1$.

The third column represents the ratio of the intensities of the various lines indicated in the (200) reflection to the intensity of the Cu $K\alpha_1$ line in the (400) reflection, with the exception of Ta $L\alpha_1$ which was compared with (400) of the same element. The last column gives the ratios, for the various wave lengths, of the corresponding 'integrated reflections', calculated with formulas due to Darwin, as stated, e.g., by Bragg, James & Bosanquet (1921), for a large mosaic crystal. This integrated intensity is written

$$\varrho = N^2\lambda^3 f^2 e^4/(2\mu m^2 c^4)\times\{(1+\cos^2 2\theta)/(2\sin 2\theta)\}\ .$$

It refers to quite a different experimental procedure, and while one calculated value of ϱ could not be applied here, it should be expected that the ratio of two of them, as used in column five would turn out to be of the same order as our observed values. It may be seen from Table 1 that this is so, although a small difference in the values chosen for f would make a considerable difference in the value of ϱ for the (200) reflection, where the f's for Ca^{2+} and 2 F^- are subtracted. It is certain, however, that these two f's are very nearly equal for the (200) reflection.

Since we are using only the ratio of this expression for one wave length in the (200) reflection to another with a different wave length in the (400) reflection, the only variables to be recorded in the ratio are θ, f, and, when the wave length passes the absorption edge of calcium, a sudden jump in the value of μ. We may, therefore omit the constants N, e, m, and c. The F-values for Ca^{2+} and 2 F^- were taken from James & Brindley (1931) by interpolating in curves drawn from their f values. Since the reflections were always from the (100) face, $\sin\theta/\lambda = 1/d = 0{\cdot}183$ for the (200) reflections and 0·367 for the (400). The f values thus selected from the curves were: for (200) $Ca^{2+} = 14{\cdot}45$, $2\,F^- = 14{\cdot}00$. For the (400) reflection, $Ca^{2+} = 10{\cdot}05$, $2\,F^- = 7{\cdot}88$. The atomic scattering factors were considered to be complex quantities and were treated after the manner of Coster & Knoll (1933). The coefficient of absorption appearing in the denominator may be taken proportional to λ^3, thus making it possible to regard λ^3/μ as constant for the different wave lengths, with the provision that when the absorption edge of calcium is passed the appropriate factor for the absorption jump must be introduced for the (200) reflections. In the vicinity of the absorption edge, the K electrons, assumed from Larsson (1929) to be 1·5 in number, were considered separately in the formula

$$f_K = 1{\cdot}5\left\{1+\frac{\ln(1-x^2)}{x^2}+\frac{i}{x^2}\right\}.$$

In the (200) reflections we must take Ca–2 F, while in the (400) it is Ca+2 F. The frequency for all electrons of both calcium and fluorine, other than the K electrons of calcium, is so far from the frequency of the Ca K absorption edge that the anomalous effect for them was disregarded.

From Table 1 it appears that there is a rise in the intensity of the observed (200) reflections in the vicinity of 1300 X.u. as we go towards lighter elements. The previous work cited was done with wave lengths considerably shorter, and our experiments agree that such reflections are very weak. From a wave length of about 1500 X.u. to the absorption edge of calcium, the intensity ratio $(200)/(400)_{\mathrm{Cu}}$ runs from 0·02 to 0·05. It is not evident that there is present the large increase in reflecting power indicated by the formula near the short wave length side of the edge. Unfortunately, there are no $K\alpha$ lines lying very near to the K edge of calcium on the short wave length side to allow an experimental test in this narrow region.

On the long wave length side of the edge the nearest $K\alpha$ line is Ca $K\alpha$, some 300 X.u. away. Therefore some photographs were taken of the Te $L\alpha_1$, the Ca $K\beta_1$, and the Te $L\beta_1$ lines, whose wave lengths are, respectively, 3282, 3083, and 3070 X.u. The last two of these lines lie quite near the K absorption edge of Ca, which was taken to be 3060 in the fluorite crystal. Since these were not $K\alpha_1$ lines the estimated value of the reflected intensity becomes more uncertain when compared with the Cu $K\alpha_1$ line, and they are not included in Table 1. It is evident, however, that they all show comparatively very strong reflection in this region on the immediate long wave length side of the edge. In fact, the increase in the reflecting power is about what would be calculated from the change in absorption coefficient as the edge is passed.

The last line of Table 1 represents a test of the (600) reflection compared with the (400) for the Cu $K\alpha_1$ line. It was judged to be stronger than the (200) for this line. MacInnes and Shedlovsky (1926) found it to be slightly less than the (200) for the shorter wave length they used. The calculated value shows the (600) to be the stronger.

The conclusion is that the reflecting power of fluorite in the (200) reflection from the (100) face is much greater in the region from 1300 to 3000 X.u. than has been reported for shorter wave lengths, and increases on passing to the long wave length side of the K edge of calcium about as one would expect because of the absence of K photoelectric absorption on that side.

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The Crystal Structure of the Intermetallic Compound $Mg_3Cr_2Al_{18}$*

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A complete determination of the crystal structure of the ternary phase (*E* phase) in the magnesium–aluminum–chromium system with composition $Mg_3Cr_2Al_{18}$ has been carried out with use of intensity data obtained from single crystal Weissenberg photographs. The refinement of the structure was carried out by application of the method of least squares. The space group is O_h^7–$Fd3m$ with 184 atoms per unit cube. The lattice constant determined with use of powder samples was $a_0 = 14\cdot53 \pm 0\cdot01$ Å. The truncated tetrahedron, the icosahedron and the hexagonal prism are prominent coordination polyhedra in this structure. An analysis of these polyhedra reveals that in places where interaction between the atoms of the transition element (chromium) and those of the hypoelectronic elements aluminum and magnesium are to be expected, the packing of the atoms is very efficient, whereas in places where such interactions are less likely the packing of atoms appears to be normal or rather loose.

Introduction

In his examination of the magnesium–chromium–aluminum system Erdmann-Jesnitzer (1940) observed a ternary intermetallic compound, the *E*-phase, with the approximate composition $MgCrAl_8$. Little, Axon & Hume-Rothery (1948) found that the composition of the *E* phase is not sharply defined but varies over a certain range and that, furthermore, zinc is soluble in the phase to some extent. Crystals extracted from two ternary alloys were found on analysis to have the compositions $Mg_2Cr_{1\cdot3}Al_{16\cdot1}$ and $Mg_2Cr_{1\cdot3}Al_{17\cdot6}$ and those from a sample containing some zinc were found to have the composition $Mg_2Cr_{1\cdot01}Zn_{0\cdot04}Al_{10\cdot9}$. In their phase diagram the point corresponding to the formula Mg_2CrAl_{13} is approximately at the center of the single-phase field of *E*.

Little *et al.* (1948) reported that the crystal structure of *E* is cubic with a lattice spacing $a_0 = 14\cdot65$ kX. ($= 14\cdot68$ Å) but that a_0 is not constant but varies over a certain range. They suggested that the unit cell contains sixteen formula units of Mg_2CrAl_{12} but they did not determine the positions of the atoms.

In a previous paper (Samson, 1954) the crystal structure of the *E* phase was briefly described. The atomic positions with the positional parameters in an early stage of the refinement were given. A more detailed description of the structure determination and the final results of the refinement will be given below.

Experimental work

Preparation of single crystals

Ternary alloys containing magnesium, chromium and aluminum and quaternary alloys containing in addition some zinc were prepared by melting pieces of the pure metals together in alundum crucibles by induction heating. During the preparation the alloys were kept in argon gas at atmospheric pressure. The melts were allowed to solidify at varying cooling rates. Some alloys were subsequently annealed for about a month at 460 °C. in evacuated and sealed pyrex tubes. At the time the previous paper (Samson, 1954) was published attempts to prepare single crystals of a size convenient for single-crystal X-ray photography from ternary magnesium–chromium–aluminum alloys had not been successful. For that reason crystals had to be isolated from a quaternary alloy containing some zinc. However, during subsequent preparative work some single crystals were obtained from a ternary alloy (approximate composition: Mg, 15%; Cr, 3%; Al, 82%) and in a slowly cooled and subsequently annealed quaternary alloy (approximate composition: Mg, 15%; Cr, 3%; Zn, 3%; Al, 79%) many well developed octahedral crystals comparatively large in size were found and isolated.

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