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0 0 0 0 3 7 0 7 6

OPTICAL ZEEMAN SPECTRA OF Am^{3+}, Cm^{3+}, AND Nd^{3+} in CaF_2*

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ABSTRACT

The optical Zeeman rotation spectra were taken of some selected transitions in Am^{3+}, Cm^{3+}, and Nd^{3+} embedded in CaF_2. Only symmetry sites arising from tetragonal compensation could be positively identified, although there was evidence for the existence of lower symmetries.

0 0 0 0 3 7 0 7 7

I. INTRODUCTION

When small amounts of rare earth ions are incorporated into CaF_2, they replace the calcium ions; however, since they are most stable in the trivalent state, a valence mismatch occurs which must be compensated. Several different charge compensation mechanisms may occur which depend upon the growth conditions, impurity concentrations and thermal treatments of the sample.[1]

In oxygen-free crystals, the most common trivalent rare earth site is one of tetragonal (C_{4v}) crystal-field symmetry. Charge compensation is attained by the presence of a F^- ion in one of the six nearest-neighbor interstitial sites. The crystal field symmetry axes are the [100] crystallographic directions. A crystal field of trigonal symmetry (C_{3v}) can arise if the fluoride ion enters into one of the eight second-nearest-neighbor interstitial positions.[2] The symmetry axes are the [111] crystallographic directions. It is also possible for the charge-compensating interstitial fluoride ion to be located far from the rare earth ion, leaving it in a field which is essentially cubic.

If oxygen is allowed to enter the crystal several new means of charge compensation are possible. The most common mechanism gives rise to a new trigonal (C_{3v}) symmetry about the rare earth ion.[3] It is believed that O^{2-} ions replace lattice fluorides at one of the eight cube corners surrounding the rare earth, resulting in an asymmetry about the body diagonal of the cube. Lower symmetries involving pairs, triads and higher order clusters of rare earth ions have been suggested by Amster and Wiggins.[4]

Several methods of analysis of the optical spectra of rare earth ions in CaF_2 have appeared in the literature, the most fruitful of these involves the Zeeman effect.

The Zeeman effect in the optical spectra of RE^{3+}-CaF_2 crystals was first observed by Arkhangelskaya and Feofilov[5] and was used to determine the position of the O^{2-} compensator in the CaF_2 unit cell. Tetragonal charge compensation was found by Crozier[6] in Ce^{3+}-CaF_2 and independently by Starostin.[7] Masui and Ibuki[8] used a pulsed magnetic field up to 130 kG to study two intense trigonal lines, probably due to O^{2-} compensation, in Pr^{3+}-CaF_2. In what has probably been the most complete analysis to date, Rector, Pandey, and Moos[9] found tetragonal sites in Er^{3+}-CaF_2 by a study of the Zeeman pattern of the lines as a function of rotation about the [110] axis of the crystal. This technique is of general applicability and has been used in this laboratory to study Nd^{3+}, Am^{3+}, and Cm^{3+} in CaF_2.

0 0 0 0 3 7 0 7 5 7 8

II. EXPERIMENTAL

A superconducting magnet was used to study the Zeeman effect. The magnet was built at this laboratory with NbTi 248B ribbon wire obtained from Supercon, on a stainless steel core form 1-7/8" i.d., 6-1/2" o.d., and 2-5/16" thickness. The coil goes normal at 130 A. with a maximum field of 67 kG.

The coil was encased in a cylindrical stainless steel dewar which could hold 20 liters of liquid helium for approximately 36 hours. It was equipped with four quartz windows very similar to those designed by Mollenauer et al.[10] except the Cu-quartz seal is made with Dupont Adiprene L-100. The window assembly is mounted to the dewar wall by means of an Indium wire gasket.

Oriented crystals were mounted in Cu-quartz housekeeper tubes which were in turn connected to a 5' stainless steel rod. The sample was then lowered into the coil from the top of the dewar. The rotation axis was parallel to the given crystal direction and perpendicular to the magnetic field.

Oriented CaF_2 crystals containing Am^{3+} and Cm^{3+} were grown in this laboratory using the Bridgman-Stockbarger technique. The concentration of dopant ion was determined only by the amount of rare earth added to the charge. This varied from 0.01 - 0.8 wt.%; however, this is known to be inaccurate because of losses during crystal growth and only gives an order of magnitude estimate. Crystals drawn from known amounts of neodymium were obtained from Optovac, Inc.[12]

High resolution measurements were made photographically using a 3.4 meter Jarrell-Ash plane grating spectrograph, Model 7102. A 300 grooves/mm grating with a peak intensity at approximately 59°, or 57,000 Å, was used in the 6-13 order range. The order of interest was isolated by means of filters. A thorium electrodeless discharge lamp was used for the reference spectrum.

III. DISCUSSION OF RESULTS

A. Americium

The electronic configuration of trivalent Am is $5f^6$ which makes it the only ion to be studied here which is not Kramer's degenerate. Since the ground state is a singlet, $^7F_0$, the Zeeman splittings of the excited states may be observed directly. The most intense transition occurs at approximately 20,000 cm^{-1} (5000 Å) and corresponds to a transition to an excited state with J = 6. This state has predominantly $^5L_6$ character mixed with some $^5G_6$.[13]

It was possible to obtain the optical Zeeman rotation pattern for only one Am^{3+} absorption line. The other lines were either too weak, too broad, or did not exhibit any splitting. The observed [110] rotation pattern for the absorption line at 5223 Å is shown in Fig. 1. From this angular variation it has been shown that the site symmetry of the line is tetragonal.[9] Note that there are only two lines (since 2 of the 3 inequivalent tetragonal sites remain magnetically indistinguishable in rotations about the [110] axis) and that their behavior is not identical. Whereas successive minima are equal, the maxima alternate in magnitude. Also, there is a 70°-110° split between those angles at which the tetragonal lines merge. This rotation pattern, however, shows an asymmetry which cannot be explained unless it is assumed that another tetragonal line lies nearby. In this case the magnetic splitting of the absorption lines would be of the same order of magnitude as the Stark splitting and the first order Zeeman approximation would not be sufficient.[14] This explanation is indeed feasible since four weak Am^{3+} absorption lines were observed 2.4, 2.7, 5.1, and 12.4 cm^{-1} from the intense line.

Although only a single line could be investigated, valuable information was gained about the thermoluminescence of Am. This absorption line at 5223 Å

0 0 0 0 3 7 0 7 9

corresponds to one of the high temperature thermoluminescence emission lines observed by Edelstein, Easley, and McLaughlin,[15] and hence confirms Merz and Pershan's[16] proposal that such thermoluminescence is due to tetragonal sites.

B. Curium

The electronic configuration of Cm^{3+} is $5f^7$. The ground state is nominally $^8S_{7/2}$ and the first excited state is $^6P_{7/2}$ at approximately 6000 Å. The absorption spectrum is very weak and only one line at 6063.2 Å was intense enough to follow. Its [110] rotation pattern is shown in Fig. 2. Although all of the Zeeman components do not unambiguously form a pattern, the bottom group of lines form a pattern characteristic of tetragonal symmetry.

The fluorescence and thermoluminescence spectra of Cm^{3+} were reported previously.[17] Unfortunately only the 6063.2 Å line, the same one used in the absorption spectrum, could be followed in fluorescence. This tetragonal line was not seen in the low temperature thermoluminescence, which is consistent with the proposed mechanism for the oxidation-reduction reactions in these crystals.

C. Neodymium

The site symmetries of Nd^{3+} in CaF_2 have been investigated mainly by electron paramagnetic resonance. Bleaney, Llewellyn and Jones[18] observed Nd^{3+} in tetragonal sites with $g_{\parallel} = 4.412$ and $g_{\perp} = 1.301$. Kask and co-workers[19] later observed two kinds of orthorhombic symmetry in addition to tetragonal symmetry. They found that the intensity of the orthorhombic symmetry increases with Nd^{3+} concentration. Vincow and Low[20] have observed Nd^{3+} in cubic sites.

There have also been a number of investigations of the optical spectrum of Nd^{3+}-CaF_2. Kiss[21] attempted to compare the observed absorption spectrum with

the theoretical spectrum based on the assumption of a cubic field. Voronko et al.[22] analyzed the optical spectrum of Nd^{3+}-CaF_2 by the concentration series method and were able to group together lines belonging to three different sites. The actual assignments of the symmetries were based on correlations with EPR data.

Crystals of Nd^{3+}-CaF_2 containing from 0.01 - 0.3 wt.% Nd were obtained from Optovac, Inc. The following is a study of the Zeeman effect on some selected transitions.

1. $^2H_{11/2}$

The $^2H_{11/2}$ manifold occurs at $\sim$ 16,000 cm^{-1} (6250 Å). For the 0.01 and 0.03 wt.% crystals, only one intense absorption line (6263.2 Å) is present. The rotation pattern of this line is not complete--some Zeeman components are either missing or weak at these concentrations. In order to intensify these weak components, a more concentrated crystal (0.3 wt.%) was studied. The optical rotation pattern for this crystal is shown in Fig. 3. Instead of the 6263.2 Å line becoming more intense, it decreased slightly in intensity and a new line at 6253.5 Å grew in. The pattern of the 6263.2 Å line is still not complete but obviously is tetragonal. The line at 6253.5 Å is not tetragonal but exhibits an extremely complex rotation pattern suggestive of a low crystal symmetry.[23] This line could possibly be orthorhombic (C_{2v}) since the EPR measurements of Kask et al.[19] showed that at low concentrations the tetragonal symmetry predominates, but the intensity of the orthorhombic signal increased with the Nd^{3+} concentration.

2. $^4S_{3/2}$; $^4F_{7/2}$

The Zeeman rotation spectra for the absorption lines at ∿ 7300 Å are shown in Fig. 4. At first glance it would seem that the patterns are almost ideal. Only a few Zeeman components are missing and all of the lines can be fit on well-shaped tetragonal patterns. Two zero field absorption lines at 7262.0 Å (13767 cm^{-1}) and 7267.2 Å (13757 cm^{-1}) split into four tetragonal patterns. Thus the transitions to both Zeeman components of the excited state are well-defined. The relation of the zero field lines to the Zeeman components can be seen in Fig. 5. This shows the splittings of the lines as a function of magnetic field strength. Note that the Zeeman components of the two tetragonal lines repel one another as the magnetic field is increased. This can happen with closely spaced Stark levels in a large enough magnetic field. The effect of this interaction on the rotation patterns can be seen in the asymmetry of the patterns about the zero field lines.

In addition to the lines at 7262 and 7267 Å, another tetragonal line was found at 7356 Å. These assignments confirm the work of Voronko et al.[22] who, using the concentration series method, assigned lines at 7267 and 7256 Å to tetragonal site symmetry.

3. $^2H_{9/2}$; $^4F_{5/2}$

Only one absorption line at 7962 Å (12556 cm^{-1}) could be followed in this spectral region. Although the symmetry is obviously tetragonal, the pattern is not ideal. This line probably corresponds to the tetragonal line at 7960 Å reported by Voronko et al.[22]; however, they reported another nearby line at 7264 Å whose symmetry is orthorhombic.

IV. CONCLUSIONS

The optical Zeeman rotation patterns have been taken of CaF_2 crystals containing Am^{3+}, Cm^{3+}, and Nd^{3+}. In all three crystals only sites arising from tetragonal compensation could be positively identified, although there was evidence that lower symmetries exist at high concentrations of Nd^{3+}. Only one tetragonal line could be identified for Am^{3+}-CaF_2 and for Cm^{3+}-CaF_2; five tetragonal lines were identified for Nd^{3+}-CaF_2. These results are consistent with the proposed mechanism for site symmetry changes and oxidation-reduction reactions for actinide ions CaF_2.[17]

0 0 0 0 3 7 0 7 8 0

FOOTNOTES AND REFERENCES

*Work performed under the auspices of the U. S. Atomic Energy Commission.

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0 0 0 0 3 7 0 7 5 8 1

FIGURE CAPTIONS

Fig. 1. Optical Zeeman rotation pattern for Am^{3+}-CaF_2, rotation about [110] direction.

Fig. 2. Optical Zeeman rotation pattern for Cm^{3+}-CaF_2, rotation about [110] direction.

Fig. 3. Optical Zeeman rotation pattern for 0.3 wt.% Nd^{3+}-CaF_2, rotation about [110] direction ($^2H_{11/2}$ manifold).

Fig. 4. Optical Zeeman rotation pattern for 0.1 wt.% Nd^{3+}-CaF_2, rotation about [110] direction ($^4S_{3/2}$; $^4F_{7/2}$ manifold).

Fig. 5. Splitting of absorption lines as a function of magnetic field strength ($^4S_{3/2}$; $^4F_{7/2}$ manifold).

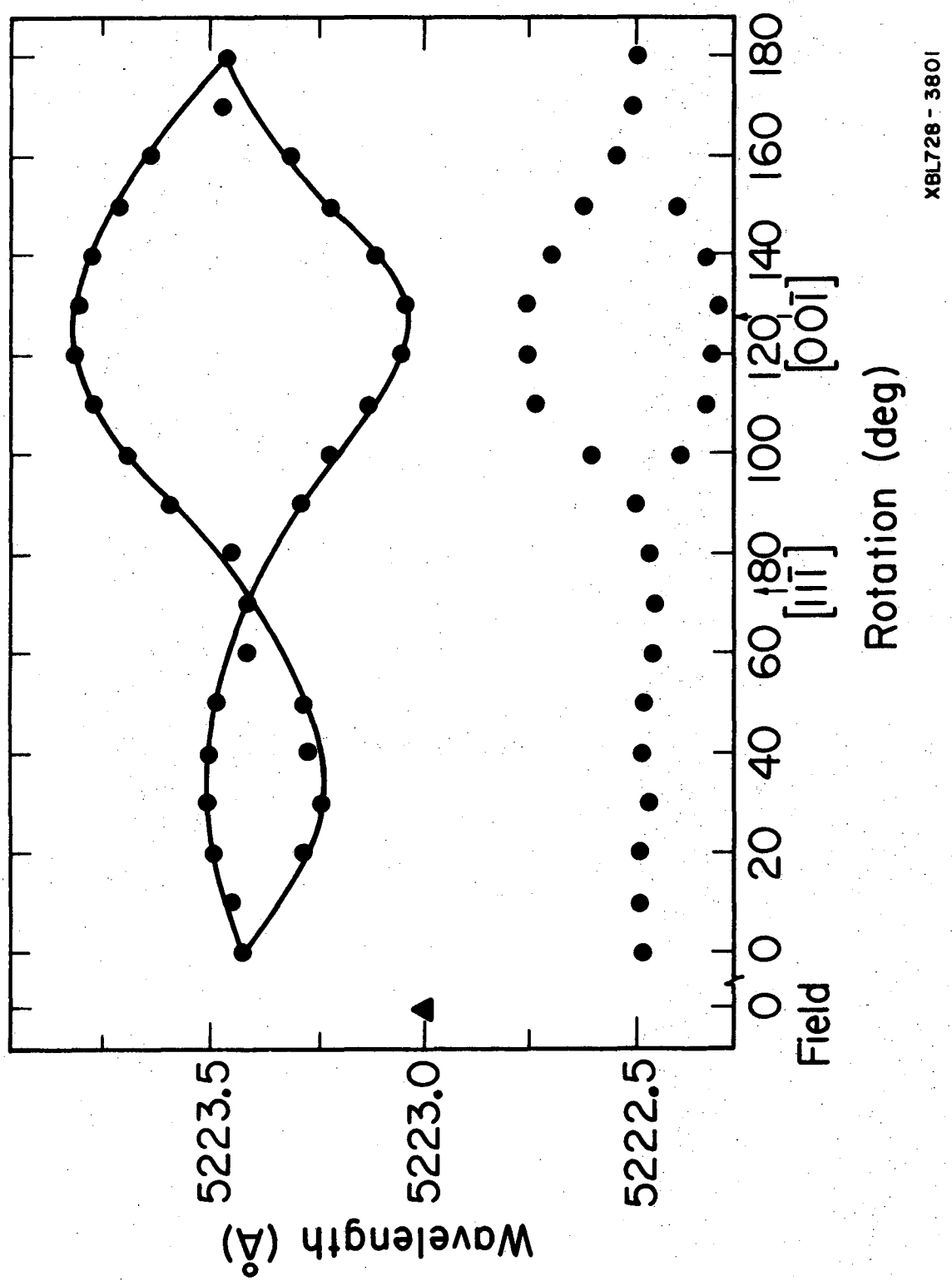
Wavelength (Å)
5223.5
5223.0
5222.5
Field
0 0 20 40 60 180 100 120 140 160 180
[111]
[001]
Rotation (deg)
XBL728-3801

Fig. 1

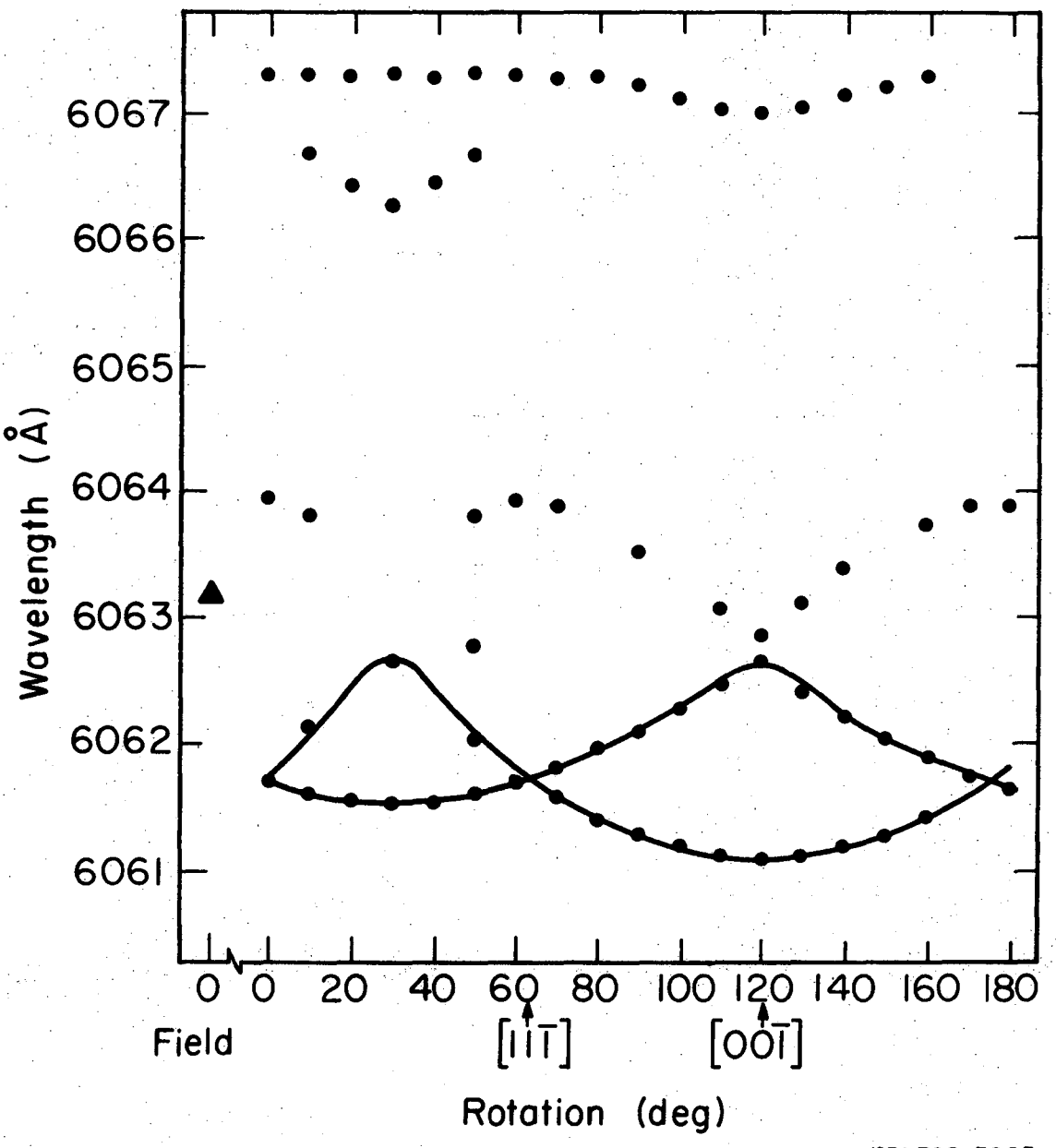
6067
6066
6065
6064
6063
6062
6061
Wavelength (Å)
0 0 20 40 60 80 100 120 140 160 180
Field
[11$\bar{1}$]
[00$\bar{1}$]
Rotation (deg)
XBL728-3805

Fig. 2

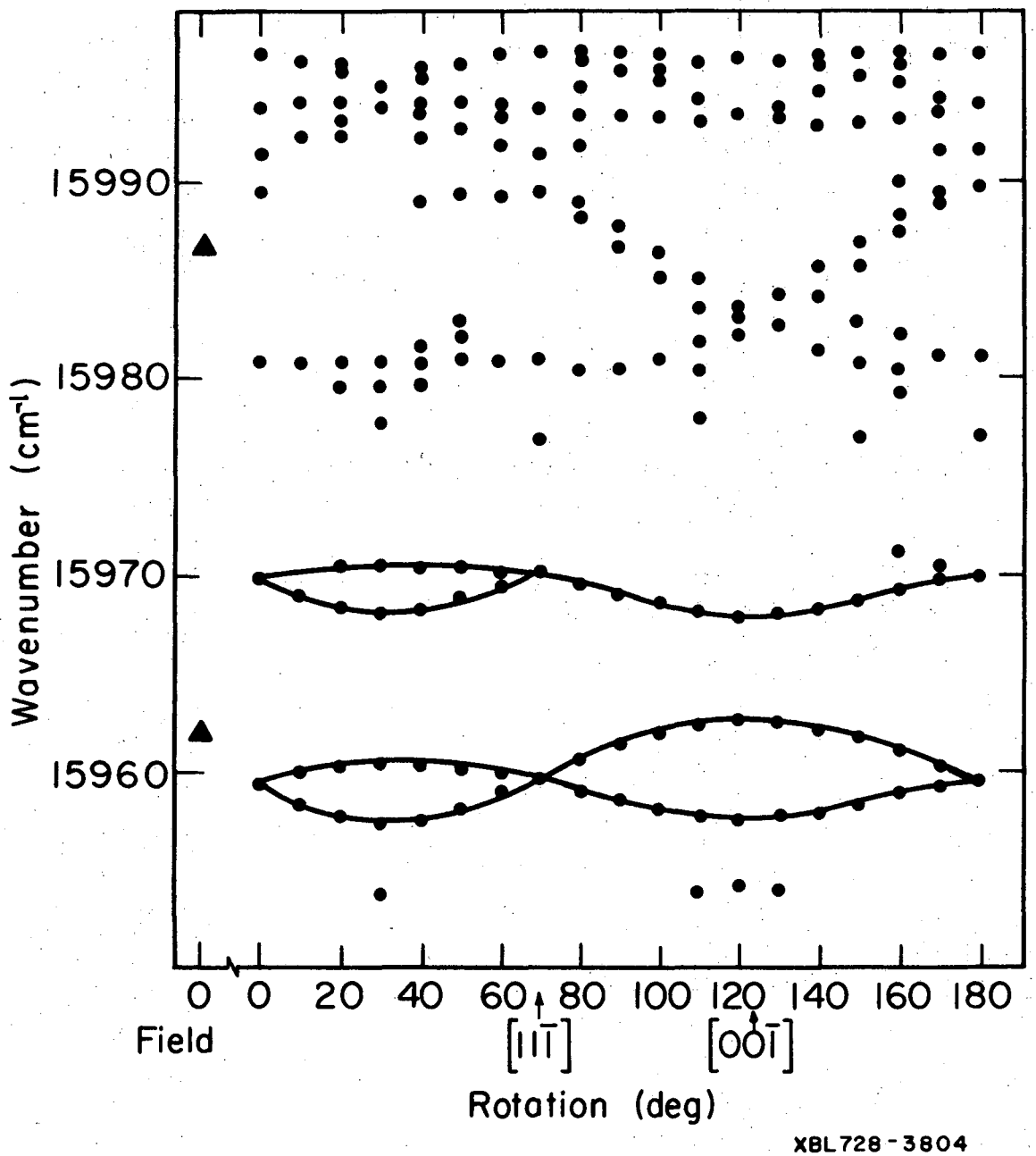
15990
15980
15970
15960
Wavenumber (cm⁻¹)
0 0 20 40 60 80 100 120 140 160 180
Field
[11$\bar{1}$]
[00$\bar{1}$]
Rotation (deg)
XBL728-3804

Fig. 3

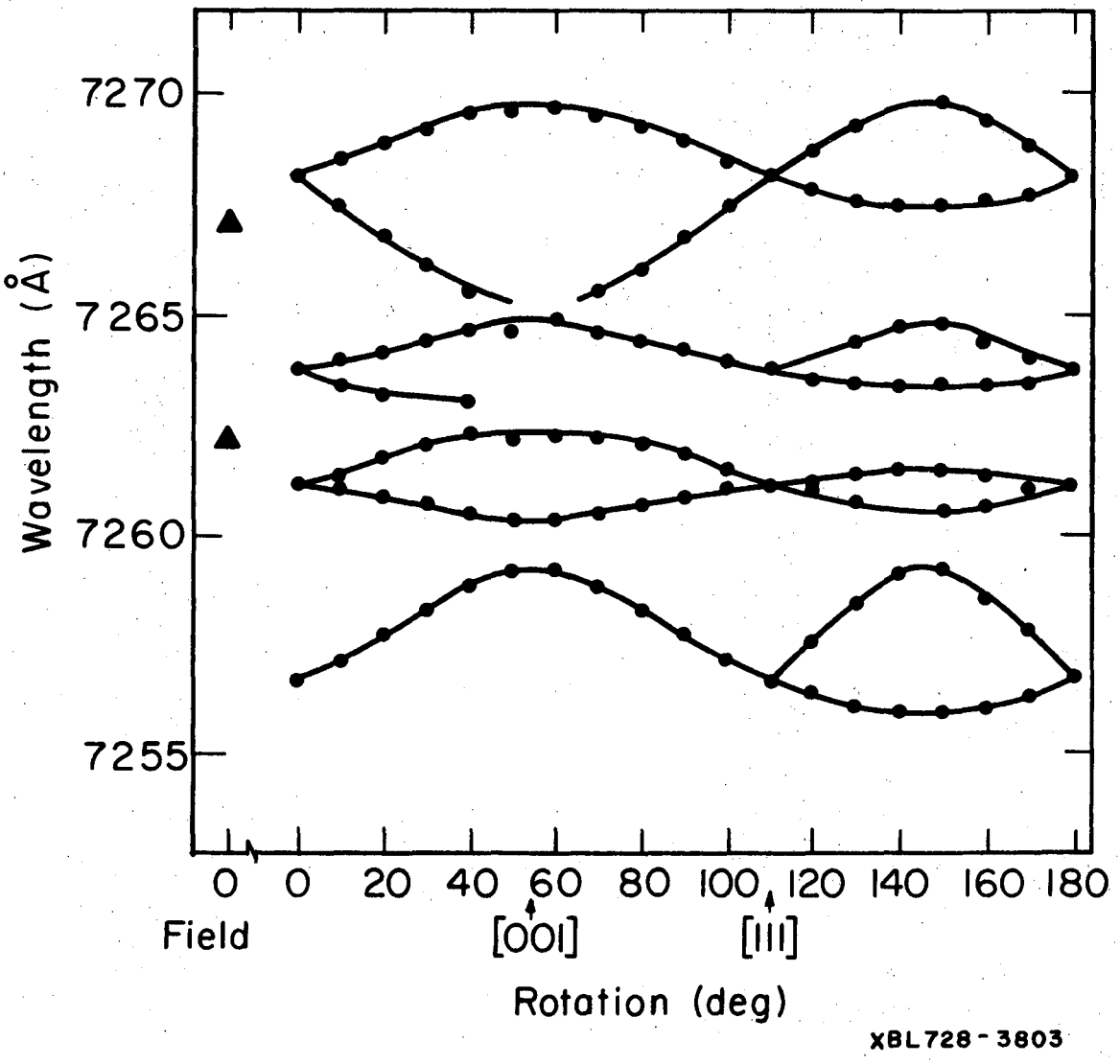
7270
7265
7260
7255
Wavelength (Å)
0 0 20 40 60 80 100 120 140 160 180
Field
[001]
[111]
Rotation (deg)
XBL728-3803

Fig. 4

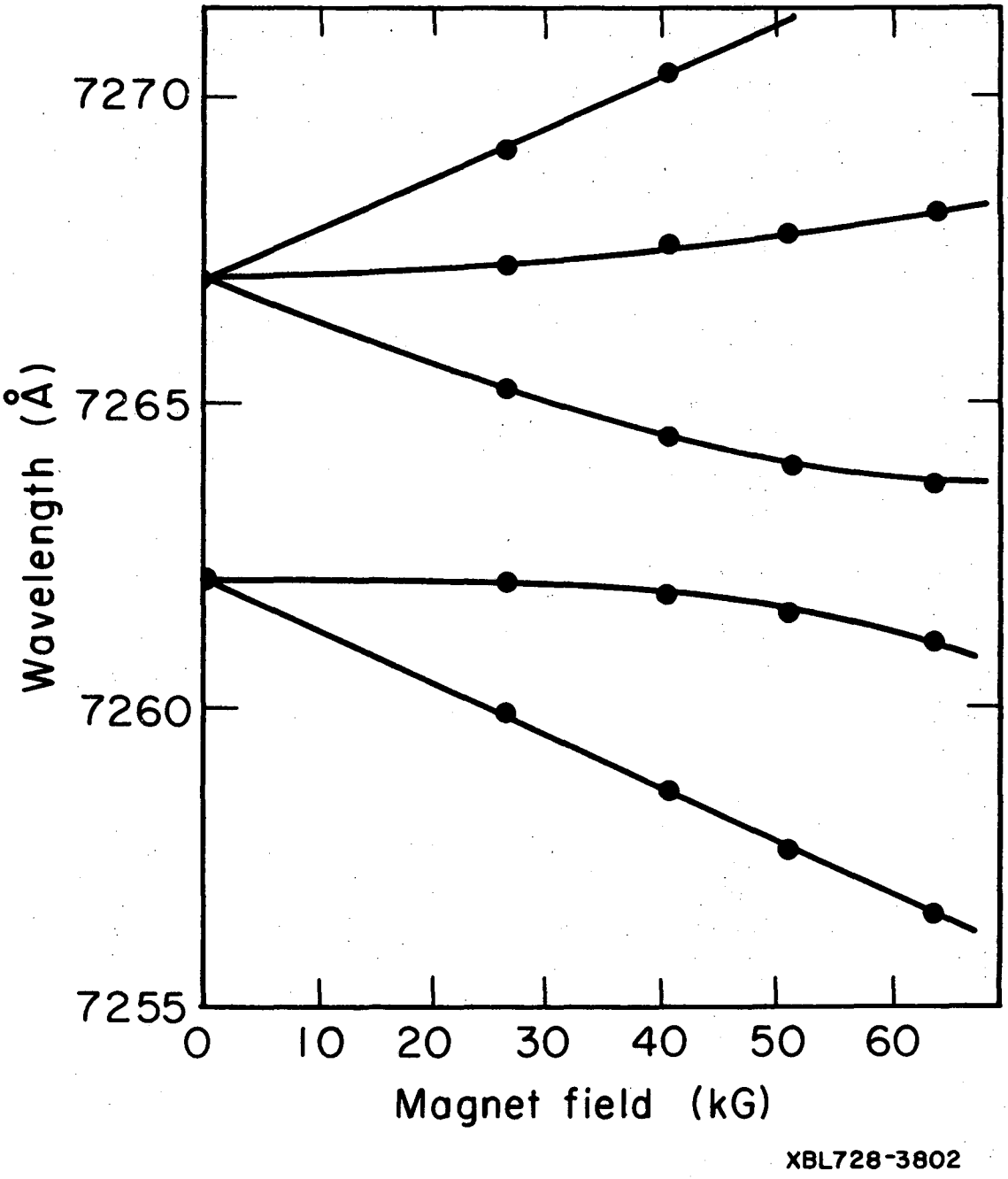
7270
7265
7260
7255
Wavelength (Å)
0
10
20
30
40
50
60
Magnet field (kG)
XBL728-3802

Fig. 5

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