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Fluorescent Spectra of Sm²⁺ in KCl. I. Evidence for C_{2v} Site-Symmetry Origin of $^7F_3$ Lines*

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In a recent publication Fong claimed a C_s site-symmetry origin for certain lines in the $^7F_3$ and $^7F_4$ regions (corresponding to transitions $^5D_0 \to {}^7F_3$, $^7F_4$) of the fluorescent spectrum of Sm²⁺ in KCl. The present authors point out that the evidence cited for the lines in the $^7F_4$ regions (8128.0 and 8122.5 Å) is inconclusive and present experimental proof that both his data as presented and the curves fitted to the data for the lines at 7693.5 and 7694.5 Å are incorrect. Arguments are also presented that the best assignment of site-symmetry origin is C_{2v}.

I. INTRODUCTION

The spectrum of Sm²⁺ doped in KCl was first studied by Bron and co-workers.[1-3] The Sm²⁺ ion goes into a K⁺ site in the cubic lattice, but different symmetries may be induced at the Sm²⁺ site, depending on the location of the K⁺ vacancy necessary to compensate for the excess charge on the Sm²⁺ ion. Bron and co-workers' assumption that most of the Sm²⁺ ions are in C_{2v} symmetry with the K⁺ vacancy at the 110 position was substantiated by a very complete explanation of the absorption and fluorescence spectra. Fong and Wong, having some doubts about the crystal field analysis, later used the Zeeman
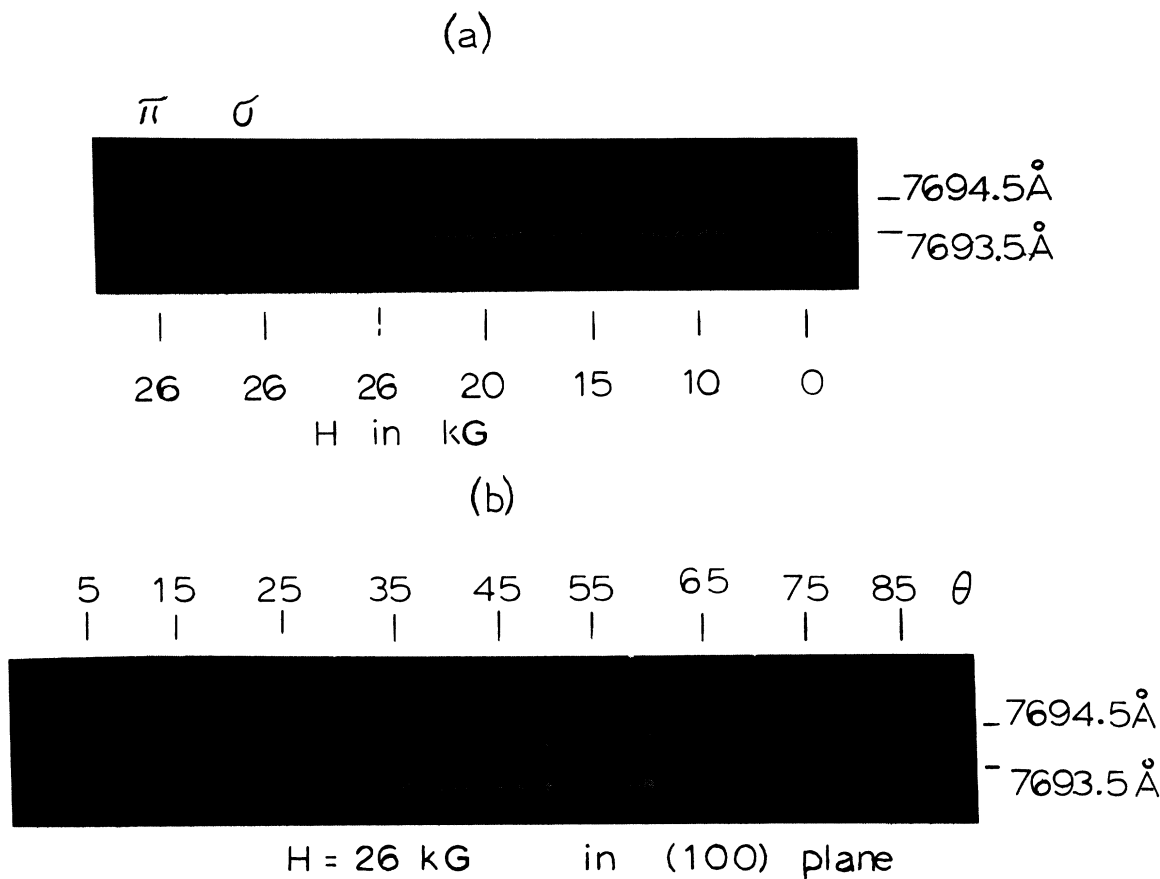
(a)

(b)

FIG. 1. Second-order Zeeman effect of $^7F_3$ fluorescent lines 7693.5 and 7694.5 Å of Sm²⁺ in KCl. (a) Magnetic field along the [100] direction, increasing from 0 to 26 kG as indicated, viewed along the [010] direction. The last two pictures show the polarization parallel (π) and perpendicular (σ) to the magnetic field at 26 kG. (b) Magnetic field rotating in the (001) plane, viewed normal to the field in the (001) plane. Note that the component which splits off from the 7694.5-Å line in (a) remains on the low-wavelength side of the 7693.5-Å line as the field is rotated in (b).

effect to demonstrate the existence of C_{4v} sites as well as C_{2v}.[4] This created the impression that Bron and co-workers were wrong in their assumption. On the other hand, the absorption spectrum appears too simple to originate from different sites. More recently, Fong and Wong have been working separately on the problem, and Wong is now convinced that Bron and co-workers were correct in their assumption. Fong went on to perform a statistical analysis of the KCl : Sm²⁺ system and showed that the concentration of various sites decreased in the order C_{4v}[200]; C_s[211]; C_{2v}[110].[5] The plates originally taken at UCLA were restudied by Fong, and several lines were identified as C_s sites.[6] In this paper the authors present their evidence that Fong erred in his identification of C_s sites.

II. IDENTIFICATION OF
7694.5- AND 7693.5-Å LINES

The best way to settle the discrepancy is by experiment. The spectrum in the $^7F_3$ region was re-

taken with a 2.5-m Ebert and a magnetic field of 26 kG. (Note: The spectral region corresponding to transitions from the $^5D_0$ level of the Sm²⁺ ions to the $^7F_3$ levels will hereafter be referred to as the "$^7F_3$ region" or alternatively as the "J = 3 region" for conciseness. This applies to all the J manifolds of the $^5D_0$ to ^7F transitions.) The spectrum was taken at third order with a plate constant of 1.6 Å/mm. Figure 1(a) shows the behavior of the two strong lines at 7694.5 and 7693.5 Å under various magnetic fields, directed along the [100] direction and viewed along the [010] direction. The strong line at 7693.5 Å is not noticeably affected by the magnetic field, while the 7694.5-Å line splits into two components. At 20 kG, one component is inside the 7693.5-Å line, and at 26 kG it appears on the other side of this line. In Fig. 2(a) of Fong's paper, [6] the component at 7693.5 Å is taken to be a component of the 7694.5-Å line, while the shorter-wavelength line is completely ignored (though reported). Figure 1 shows conclusively that this was a mistake. The

(a)

$7694.5 \overset{\circ}{A}$-

$7693.5 \overset{\circ}{A}$-

a

H = 26 kG   in (100) plane

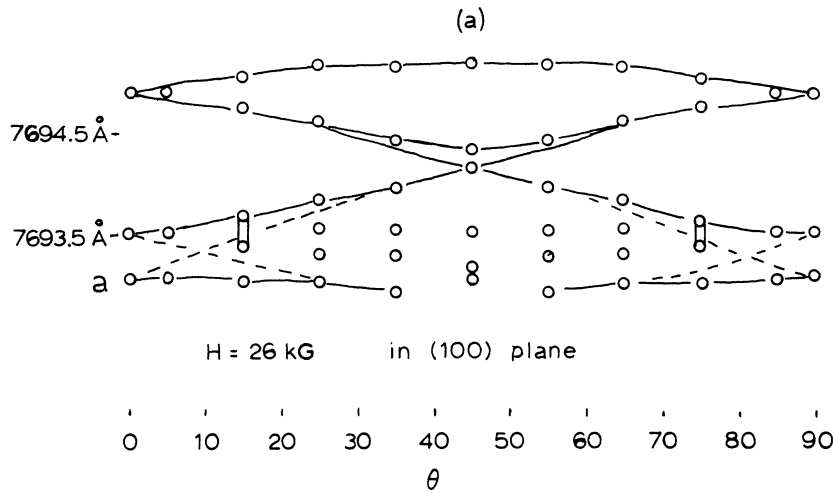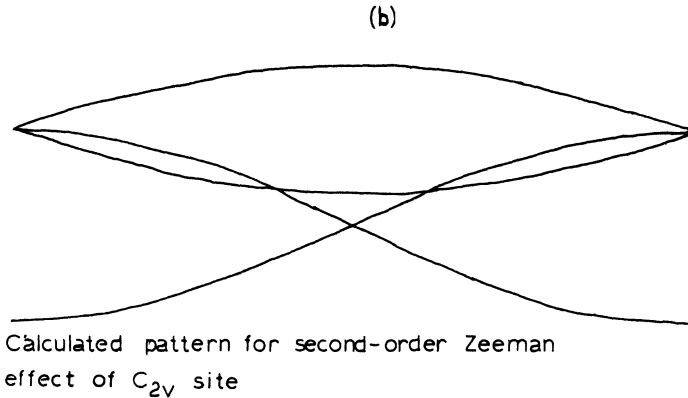0 10 20 30 40 50 60 70 80 90

θ

(b)

FIG. 2 (a) Plate reading of Fig. 1(b). The dashed line indicates the behavior that would be expected if there were no interaction between the two states responsible for the zero-field lines. (b) Typical second-order Zeeman pattern for C_{2v} site symmetry.

Calculated pattern for second-order Zeeman effect of C_{2v} site

TABLE I. (a) Parameters for second-order Zeeman effect of C_{2v} sites with $\vec{H}$ in the (001) plane. The first column lists the possible locations of the K^+ vacancy followed by the letters designating sites which are magnetically distinct for arbitrary directions of the magnetic field. The second column gives a set of crystal axes corresponding to coordinate axes at each site, and the third column gives the components of the magnetic field in the site coordinates . The last column gives polarization for electric dipole transitions under low field if $\vec{H}$ is the [110] direction and viewed along [010] when the terminal state is as indicated. The origin is assumed to be $\Gamma_1(^5D_0)$. (b) Character table of C_{2v}.

(a)

Site		Site axes			$\hat{H}=(a,\ b,\ 0)$			Weak field polarization		
		x	y	z	H_x	H_y	H_z	Γ_1	Γ_2	Γ_4
[110]	A	[$\bar{1}$10]	[001]	[110]	$(b-a)/\sqrt{2}$	0	$(a+b)/\sqrt{2}$	π	π	σ
[1$\bar{1}$0]	B	[$\bar{1}\bar{1}$0]	[001]	[1$\bar{1}$0]	$-(a+b)/\sqrt{2}$	0	$(a-b)/\sqrt{2}$	π	π	σ
[101]	C	[$\bar{1}$01]	[010]	[101]	$-a/\sqrt{2}$	b	$a/\sqrt{2}$	$\pi\sigma$	$\pi\sigma$	$\cdots$
[10$\bar{1}$]		[$\bar{1}$0$\bar{1}$]	[010]	[10$\bar{1}$]	$-a/\sqrt{2}$	b	$a/\sqrt{2}$	$\pi\sigma$	$\pi\sigma$	$\cdots$
[011]	D	[01$\bar{1}$]	[100]	[011]	$b/\sqrt{2}$	a	$b/\sqrt{2}$	σ	σ	π
[01$\bar{1}$]		[011]	[100]	[01$\bar{1}$]	$b/\sqrt{2}$	a	$b/\sqrt{2}$	σ	σ	π

(b)

	E	C_2	σ_v	σ_v'	Base
Γ_1	1	1	1	1	z
Γ_2	1	-1	-1	1	$x,\ J_y$
Γ_3	1	1	-1	-1	J_z
Γ_4	1	-1	1	-1	$y,\ J_x$

anisotropy pattern with $\vec{H}$ rotation in the (001) plane and observation path perpendicular to $\vec{H}$ is shown in Fig. 1(b). The strong line at 7693.5 Å has no Zeeman effect when $\vec{H}$ is in [100] direction, but it splits into three lines when $\vec{H}$ is in other directions. The results of the plate reading are shown in Fig. 2. One interesting point is that the shorter-wavelength component of the 7694.5-Å line, marked g, never seems to be connected with the longer-wavelength line as the magnetic field is rotated through 90°. This short-wavelength component does not interact with the no-field line at 7693.5 Å in Fig. 1(a), but it repels the 7693.5-Å line when the magnetic field is rotated from the [100] direction. The dashed line in Fig. 2 shows the position variation of the short-wavelength component if there is no interaction. [Figure 2(a) shows the typical pattern for second-order Zeeman effect of a C_{2v} level expected when there is no level crossing interacting, i.e., repulsion. The calculation of such patterns, using the magnetic field components given in Table I, is straightforward and will be discussed in detail in Paper II.] In order to verify this point, a variation of the magnetic field was carried out at [110] direction. The three short-wavelength lines approach the 7693.5-Å no-field line and the three longer-wavelength lines approach the 7694.4-Å no-field line. The repulsion shows that the two no-field lines belong to the same site.

A C_{3v} site with $\vec{H}$ along [100] could lead to only one component, as would a state with zero second-order Zeeman effect. At 45° ($\vec{H}$ along [110]) the line would be split into two components for C_{3v} sites, since for C_{3v} there are only two magnetically different sites, while the results in Fig. 1(b) or 2(a) show three components in this situation (a weak line shows in the longer-wavelength side of the strong line at 45°). This fact, as well as the repulsion effect, precludes the possibility of a C_{3v} site for the 7693.5-Å line. The repulsion requires that the two lines originate from the same ion and hence the same site symmetry. Figure 1(b) [or

Fig. 2(a)] should be compared with Fong's Fig. 2(a), particularly the behavior of the long-wavelength component in the vicinity of 45°. In Fig. 1(b), it is clearly indicated that this component is one continuous line from 35° to 55°, not two lines that drop and cross. If components crossed, the intensities would double at the crossing point. The functional behavior expected for either C_{2v} or C_s second-order patterns is not so rapidly a varying function of θ as to excuse misalignment. [The tolerance in our experiment for the differences in the 10° intervals is ± 0.5°. An estimate of the constant error (from Fig. 1(b)) is less than 1°.]

Suppose the K^+ vacancy is in the 110 position and the z axis for this site is taken as the [110] direction. Then the x, y axes are taken as [$\bar{1}$10] and [001], respectively. All other sites can be obtained by symmetry operations of the group, and the results are listed in Table I. As seen from the site components of the magnetic field when it is rotating in the (001) plane, the six equivalent sites are reduced to form magnetically different sites labeled A, B, C, and D. (Only half the sites are listed. The remainder are connected by the inversion operator to those given and are not distinguished in these experiments.) Γ_4 will show π polarization for site D, and σ polarization for sites A, B under a weak magnetic field along the [100] direction. If the magnetic field is strong, Γ_4 can mix with Γ_1 and Γ_2 through H_x and H_z, and sites A, B, and C will show $\pi\sigma$ polarization. For site D with $\vec{H}$ along its y axis, Γ_3 can mix with Γ_4 with no change of polarization since Γ_3 is a forbidden transition. This is the same as the experimental data shown in Fig. 1, and the no-field line at 7694.5 Å is identified as Γ_4 of C_{2v} site. The short-wavelength component of the 7694.5-Å line in the Zeeman pattern corresponds to site D which has the magnetic field along its y axis when $\vec{H}$ is along [100]. (See Table I.) J_y transforms like Γ_2 and by group theory Γ_4 will not have second-order Zeeman interaction with Γ_1 or Γ_2. This is the experimental result of Fig. 1(a).

8132.6 Å —
8128.0 Å —
8122.5 Å —

θ 5°   15°   25°   35°   45°   55°   65°   75°   85°
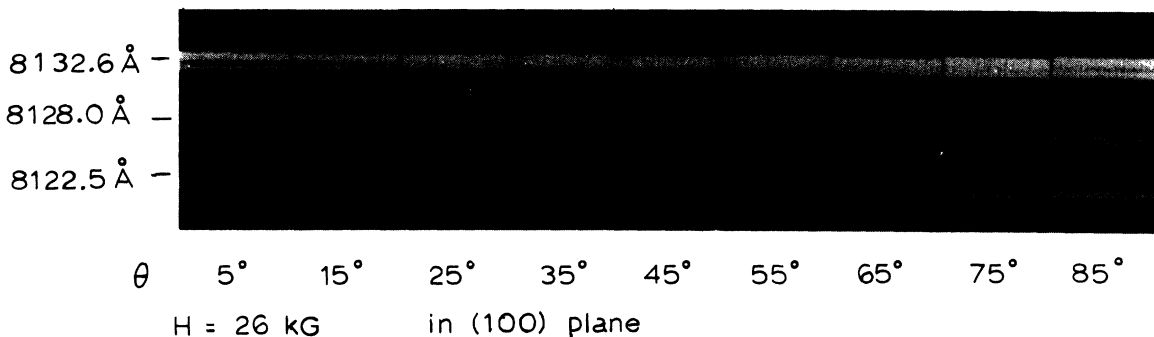
H = 26 kG   in (100) plane

FIG. 3. Second-order Zeeman effect of fluorescent lines in the $^7F_4$ region of Sm²⁺ in KCl.

When the magnetic field is rotated from the [100] direction, site D will have H_x and H_y components and there will be repulsion. Based on the experiment here, the no-field line at 7693. 5 Å can be either Γ_1 or Γ_2 of C_{2v}, which are indistinguishable in these experiments, as may be seen from Table I.

III. IDENTIFICATION OF 8128.0- AND 8122.5-Å LINES

Fong's identification of C_s sites is based on six magnetically different orientations for C_s symmetry. The second-order Zeeman effect will thus have six components. However, according to Fong's data only three components each were ever observed for the 8128. 0- and 8122. 5-Å no-field lines, as shown in Fig. 3. It is clear that his identification is not established. The lines shown in Fig. 3 are not very sharp, but the pattern for 8128. 0 Å

resembles the calculated pattern for C_{2v} given in Fig. 2(b). (These photos are from the original plates taken by Fong and Wong.[4])

IV. CONCLUSION

The data on the $^7F_3$ lines reported by Fong[6] are not reproducible, and the data obtained in the authors' experiment show there is no justification for C_s symmetry assignment to either the 7693. 5- or the 7694. 5-Å line. Moreover, the polarization results cannot be explained in terms of the C_s sites as given by Fong for any assumption of the symmetry of the terminal state or transition involved.

As we have shown, the results can be interpreted in terms of the C_{2v} [110] sites. Further evidence that the two lines originate from the same Sm^{2+} ion site will be given in Paper III in this series.

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Fluorescent Spectra of Sm²⁺ in KCl. II. Site-Symmetry Identification of Prominent Lines in the $^7F_1$ and $^7F_2$ Regions by the Second-Order Zeeman Effect, Including Polarization, Selection Rules, and Intensities*

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In a recent publication, Fong and Bellows reported results on high-magnetic-field studies of lines in the low-J-value regions of the fluorescent spectrum of KCl: Sm²⁺ and made site-symmetry assignments accordingly. The authors dispute their methods, data, and identifications on both theoretical and experimental grounds. The authors show that the results of the magnetic field experiments, including both intensity and polarization data as well as splitting, can be interpreted by assigning the prominent lines in these regions as originating from a Sm²⁺ ion in a C_{2v} symmetry site. This is in accord with the earlier work of Bron and Heller.

I. INTRODUCTION

Several years ago, Bron and Heller[1] analyzed the fluorescence spectrum of Sm²⁺ ions in KCl in order to determine the effect on the site symmetry of the Sm²⁺ ion due to the location of the K⁺ vacancy which charge compensates the doubly ionized impurity. The method used was that of polarized emission under polarized excitation.[2] Although good polarization data were obtained for the $J = 0$, 1, 2, and 3 levels only of the ^7F term, Bron and Heller decided that the prominent spectrum at 10 °K was originating from a C_{2v} nearest-neighbor 110 site.

Fong and Wong[3] speculated that other orientations of the K⁺ vacancy, leading to correspondingly different site symmetries, should be evidenced in the fluorescent spectrum. Using the first-order Zeeman effect at 4. 2 °K with magnetic fields up to 26. 5 kG, they found evidence of C_{4v} sites and an axial C_{2v} site, indicating either that the vacancy was further removed from the Sm²⁺ ion or that there simply was an accidental degeneracy. No Zeeman effect was observed in the $J = 0$, 1, and 2 regions for the field used, and the two strong lines in the $J = 3$ region were not understood. Recently Fong[4] reanalyzed the plates and claimed that the
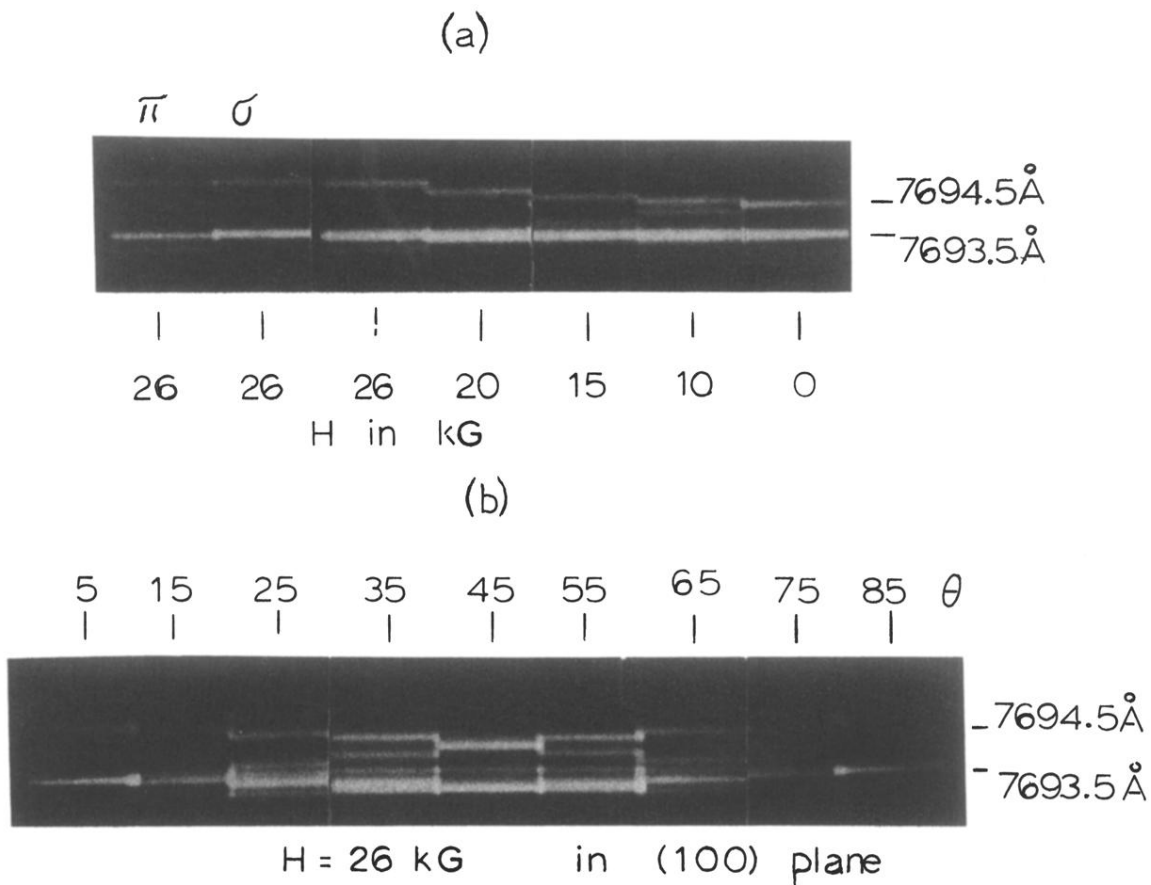
FIG. 1. Second-order Zeeman effect of $^7F_3$ fluorescent lines 7693.5 and 7694.5 Å of Sm^{2+} in KCl. (a) Magnetic field along the [100] direction, increasing from 0 to 26 kG as indicated, viewed along the [010] direction. The last two pictures show the polarization parallel (π) and perpendicular (σ) to the magnetic field at 26 kG. (b) Magnetic field rotating in the (001) plane, viewed normal to the field in the (001) plane. Note that the component which splits off from the 7694.5-Å line in (a) remains on the low-wavelength side of the 7693.5-Å line as the field is rotated in (b).
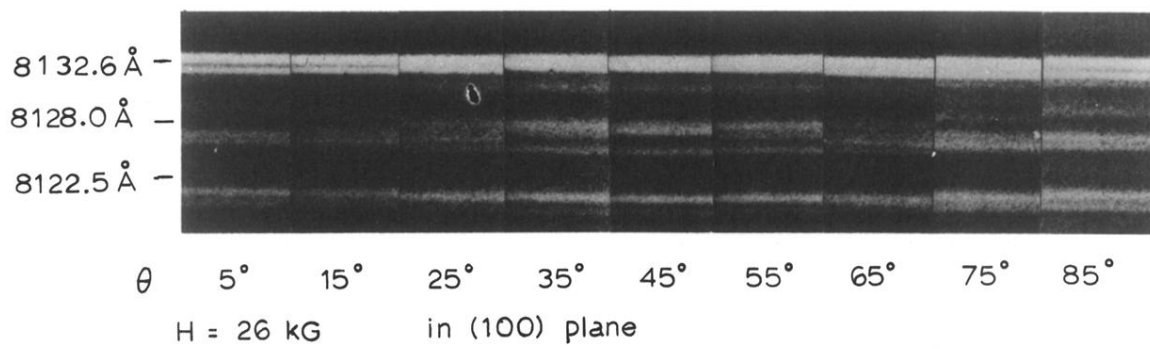
8132.6 Å —
8128.0 Å —
8122.5 Å —

θ   5°   15°   25°   35°   45°   55°   65°   75°   85°

H = 26 kG   in (100) plane

FIG. 3. Second-order Zeeman effect of fluorescent lines in the $^7F_4$ region of Sm^{2+} in KCl.