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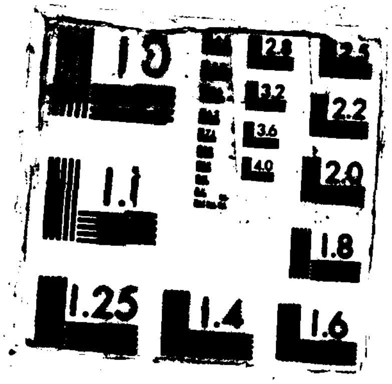
1.0
2.8
2.5
3.2
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3.6
4.0
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Optical and ESR Studies of Co^{2+}: Beta" Alumina

by

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Optical absorption and ESR spectroscopy were used to identify the site symmetry for Co^{2+} in beta" alumina. Optical absorption indicated occupancy of a tetrahedral site with D_q = 410 cm^{-1} and B = 800 cm^{-1}. There was no evidence of Co^{2+} in octahedral symmetry. ESR spectra indicated Co^{2+} in an axial symmetric site to the C-axis. This is likely to be the Beevers·Ross site which has C3v symmetry. The parameters g = 2.16 and g = 4.59 are consistent with this assignment.

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OPTICAL AND ESR STUDIES OF Co^{2+}:β" ALUMINA

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The $\overset{\text{Beta}}{\beta''}$ aluminas have recently been reported to exhibit several interesting optical properties, including lasing action.[1] The materials are doped by ion exchange reactions, and techniques for introducing numerous lanthanide and transition metal ions have been demonstrated.[2, 3] Among the transition metal ions, $\overset{\text{COBALT ION}}{Co^{2+}}$ is of interest for tunable laser systems in the infra red because of the $^4T_2 \rightarrow {}^4T_1(^4F)$ transition which occurs in an octahedral crystal field.[4] As a laser host for $\underset{\text{COBALT ION}}{Co^{2+}}$ $\underset{\text{BETA}}{\beta''}$ alumina is potentially significant because previous crystallographic studies of $\underset{\text{MANGANESE ION}}{Mn^{2+}}$ and $\underset{\text{ZINC}}{Zn^{2+}}$ $\overset{\text{Beta}}{\beta''}$ aluminas indicated that the transition metal ions occupied both octahedral and tetrahedral sites within the conduction plane.[5] In the present paper we use optical absorption and ESR spectra to help identify the site symmetry for $\overset{\text{COBALT}}{Co^{2+}}$ in $\overset{\text{Beta}}{\beta''}$ alumina.

Co^{+2} was introduced in the β" alumina structure by ion exchange reactions. [3] In this approach, single crystals of Na β" alumina (nominally, $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$) were immersed in $CoCl_2$ or in eutectic NaCl-$CoCl_2$ melts at 700 and 750 ° C. The composition of the resulting crystals was $Na_{1.67-2x}Co_xMg_{0.67}Al_{10.33}O_{17}$ (where x varied from 0.67 to 0.80) and they were colored a deep blue. The use of ion exchange reactions at these relatively low temperatures ensured that the exchanged ion (i.e., Co^{2+}) could not diffuse into the spinel blocks and thus resided within the conduction plane. There are two types of sites available for the ion; the mid-oxygen (octahedral) and the Beevers-Ross and anti-Beevers-Ross sites (both tetrahedral). It is interesting to note that when Co^{2+} was added in high temperature crystal growth studies involving β alumina [6] or β" alumina, [7] Co^{2+} occupied tetrahedral sites within the spinel block.

Optical absorption spectra were taken at room temperature over the range of 300 nm to 2500 nm using a Beckman UV 5270 spectrometer. Broad absorption bands with peak values at 580 nm and 1550 nm were observed. The former bands are in good agreement with those reported by Akridge and Kennedy. [8] Although more detailed low temperature spectra were not taken, we were still able to use these bands to estimate values for the crystal field parameters Dq and B using standard procedures. [9] In this case it was assumed, according to the blue color of the crystals, that the Co^{2+} was in a tetrahedral site and that the 583 nm and 1407 nm bands corresponded to the $^4A_2 \rightarrow {}^4T_1(^4P)$ and $^4A_2 \rightarrow {}^4T_1(^4F)$ transitions, respectively. The resulting values of $Dq = 410\ cm^{-1}$ and $B = 800\ cm^{-1}$ ($Dq/B = 0.51$) are in reasonable agreement with literature values for Co^{2+} in tetrahedral sites in other host structures. [10, 11] The agreement between the calculated and observed absorption bands are given in Table

1. The transition beyond 2400 nm could not be definitively identified in the present work. The lowering of symmetry, which is C_{3v} rather than T_d, and spin-orbit coupling would account for the splitting and shoulders observed experimentally. Finally, it is important to note that there was no evidence of absorption in the 725-750 nm range which is characteristic of Co^{2+} in octahedral symmetry. [12]

The ESR spectra were recorded on a Brucker ESR 220 D spectrometer operating at X band. Temperatures of approximately 20 K were required because of the short spin-lattice relaxation time for Co^{2+}. The ESR spectrum, taken when the magnetic field, B_o, was parallel to the c- crystal direction, consisted of a broad single line of linewidth 35 mT. In these Co^{2+} doped β" alumina samples, we did not observe any distinct lines associated with hyperfine interaction (^{59}Co, I = 7/2, 100% abundance) at this or any other orientation. When B_o rotated in a plane perpendicular to the c- axis, the spectra exhibited no angular variation. In this case there was a single line centered at 140 mT of linewidth 25 mT. The magnitude of this linewidth prevented us from directly observing hyperfine interaction. The angular variation for the ESR line when B_o was turned in a plane containing the c- axis is shown in Fig. 1. The c- axis occurs at the intensity maximum of the ESR line.

The ESR results indicate that the Co^{2+} ions reside in a single site which is axially symmetric to the c- axis. The one type of site in the β" alumina conduction plane consistent with this description is the Beevers-Ross (or anti Beevers-Ross) site, which is characterized by C_{3v} symmetry. In addition, the values $g_{\parallel} = 2.16$ and $g_{\perp} = 4.59$ are comparable to the g-tensor components reported for other hosts in which the Co^{2+} were located in sites of C_{3v} symmetry. [10, 13] One other interesting feature to note is that the magnitude of the ESR linewidth suggests that either substantial disorder exists in the crystal field along directions both perpendicular and parallel to the c-axis, or that there is substantial dipolar interaction between neighboring Co^{2+} ions which are expected to lie within 0.5 nm. [5]

The results of the optical absorption measurements are in good agreement with those of ESR. Both spectra are dominated by Co^{2+} residing in the tetrahedral site in the β" alumina conduction plane. This behavior is somewhat different from that observed for other ion exchanged transition metal β" aluminas, [5] however, it is possible that the presence of some octahedral Co^{2+} could be masked by the relatively weak oscillator strength of the Co^{2+} ion in that symmetry and the broad linewidth of the ESR spectra. Finally, it is significant to note that although Co^{2+} in β"alumina does not appear to be a potential laser system because of its strong preference for tetrahedral sites, other divalent transition-metal ions, such as Ni^{2+} or V^{2+} may prefer octahedral symmetry in β" alumina and thus be suitable activators for solid state tunable lasers. [4]

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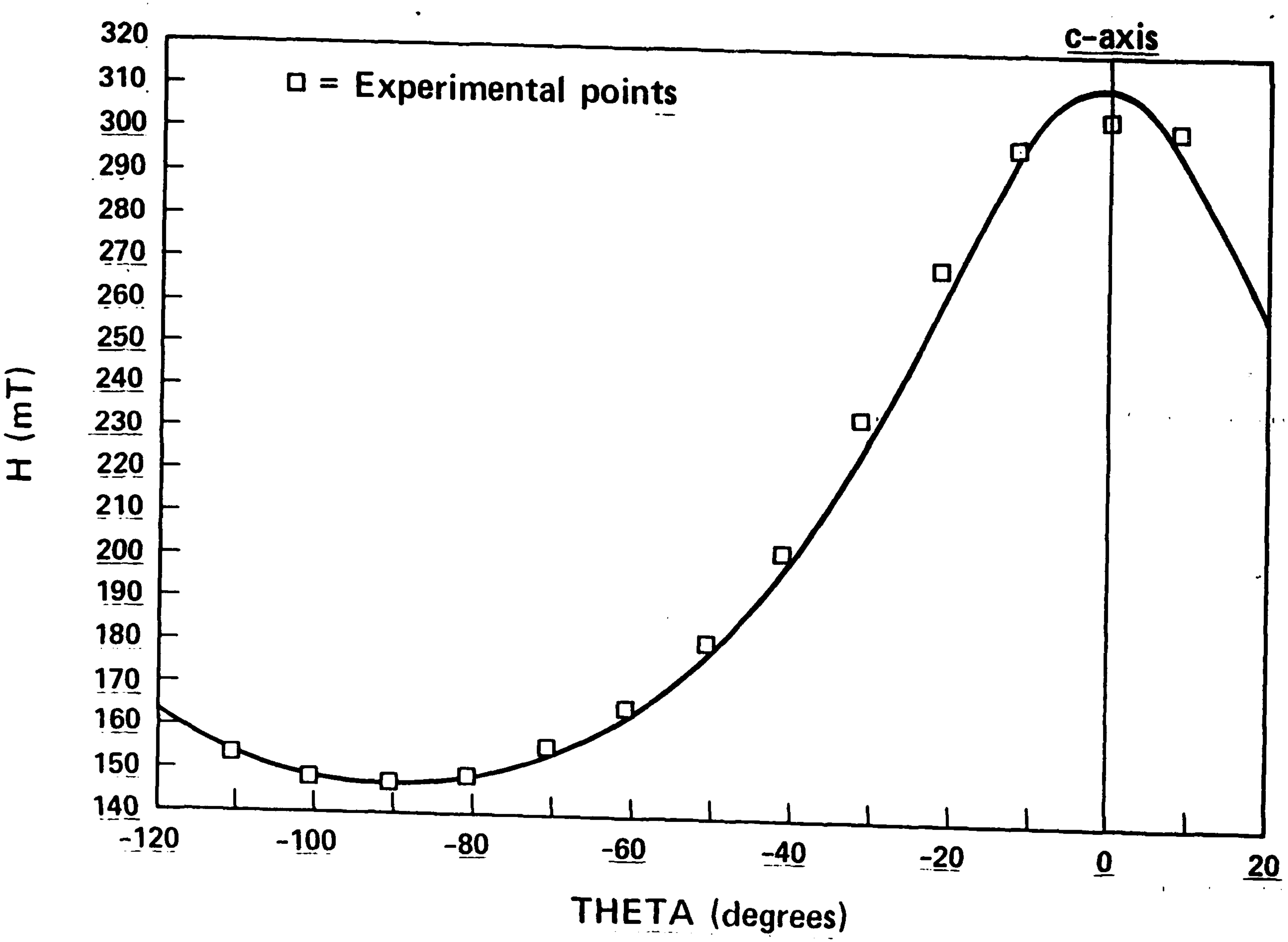
Table 1: Observed and calculated results for optical absorption. Calculated baricenter used $B = 800\ cm^{-1}$ and $D_q = 410\ cm^{-1}$

Observed Bands (nm)	Experimental Baricenter (nm)	Calculated Baricenter (nm) $B = 800\ cm^{-1}$ $D_q = 410\ cm^{-1}$
550, 580, 620	583	582
1290, 1380, 1550	1407	1407
		2439

Caption

Fig. 1 Angular variation of ESR line for B_0 turning in a plane containing the c-axis.


□ = Experimental points
c-axis
H (mT)
320
310
300
290
280
270
260
250
240
230
220
210
200
190
180
170
160
150
140
-120
-100
-80
-60
-40
-20
0
20
THETA (degrees)

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