PHYSICAL REVIEW B VOLUME 11, NUMBER 10 15 MAY 1975

Mass-action law for additive coloration of BaO[†]

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(Received 19 December 1974)

Crystals of BaO were additively colored at 100 °K intervals between 1423 and 1723 °K in Ba vapor at pressures from 7×10^{-4} to 1.7 Torr. A development of the mass-action law for the additive coloration process including complete first ionization and partial second ionization of the anion vacancies is presented. A good fit of the experimental data for the density of induced color centers, N_F, as a function of the number of Ba atoms in the vapor, N_{Ba}, was obtained using the expression $N_F^2/N_{\mathrm{Ba}} = 1.98 \times 10^{22} e^{-0.42\ \mathrm{eV}/kT}$, which assumes first ionization alone. However, a slightly better fit was obtained using a more complex expression which allows for partial second ionization of the anion vacancies. From the parameters of this fit, it was tentatively concluded that the second ionization energy E_2 plus a contribution due to changes in the thermal entropy was $E_2' = E_2 + (\Delta S_1 - \Delta S_2)T = 1.07$ eV. Using Rose and Hensley's value for the first ionization energy of $E_1 = 0.1$ eV, the formation energy for neutral-anion vacancies was found to be $E_F = 0.05$ eV. These last results should be regarded as tentative pending verification of the reliability of the barium vapor-pressure curve used.

I. INTRODUCTION

When an ionic crystal, such as an alkali halide or alkaline-earth oxide, is heated in a vapor of its metallic constituent, an excess of the metal in the form of anion vacancies (F centers) is introduced into the crystal. For the alkali halides,[1] MgO,[2] CaO,[3] and SrO,[4] this additive coloration process has been observed to obey the simple mass-action law $N_F = N_v K(T)$, where N_F is the density of color centers and N_v is the density of metal atoms in the vapor. On the other hand, from rather limited data Timmer[5] tentatively concluded that BaO obeys the relationship $N_F^3 = N_v K(T)$. His measurements did not include a sufficiently wide range of temperatures to determine the temperature dependence of $K(T)$. He suggested that this form of the mass-action law was possibly due to both electrons in the divalent color centers being released to the conduction band at the coloring temperature.

Rose and Hensley[6] showed that the color centers in BaO are partially ionized even at room temperature. However the initial attempts in the present investigation to establish the correct mass-action law for BaO were unsuccessful because of unacceptable scatter in the experimental data. Even crystals colored under what seemed to be identical conditions gave widely varying results. After an extensive investigation, it was established that in order to avoid extraneous coloration, it was not only necessary to protect the crystals from reaction with the tantalum bomb, but also from an excess of Ba vapor resulting from the rather large amount of BaO vapor from the crystal reacting with the tantalum. With these crucial modifications in the experimental procedure, good reproducible data were obtained. It was thus established that the anion vacancies are singly ionized at the coloring temperature with probably a small degree of second ionization. A brief treatment of the theory for partial second ionization is presented as no adequate treatment could be found in the literature.

II. THEORY

The problem to be considered here is the effect on the density of coloration resulting from the anion vacancies being partially or totally ionized. Since Rose and Hensley[6] concluded that the ground state of the F center in BaO was about 0.1 eV below the conduction band for thermal transitions, it will be assumed that at the coloring temperature essentially all of the anion vacancies are at least singly ionized. The degree of second ionization will be included as a dynamic variable. It will also be assumed that the density of electron traps, such as cation vacancies and certain impurities, is negligible compared with the density of the anion vacancies.

The equilibrium properties of the system may be derived from the Helmholtz free energies of the crystal F_c and the barium vapor F_v at constant volumes V_c and V_{Ba} and temperature T. The condition describing the equilibrium between the number of barium atoms in the vapor N_{Ba} and number of excess barium atoms dissolved in the crystal in the form of anion vacancies N_F (measured as the number of F centers at 77 °K) is given by

$$\left(\frac{\partial F_c}{\partial N_F}\right)_{V_c,\,T} = \left(\frac{\partial F_v}{\partial N_{\mathrm{Ba}}}\right)_{V_{\mathrm{Ba}},\,T} . \qquad (1)$$

If X is the number of doubly ionized anion vacancies, then the condition describing the equilibrium between the number of electrons in the conduction band $N_F + X$ and the number of electrons trapped in oxygen vacancies $N_F - X$, is

$$\left(\frac{\partial F_c}{\partial X}\right)_{V_c,\,T} = 0 . \qquad (2)$$

The Helmholtz free energy of the barium vapor may be written

$$F_v = -N_{\mathrm{Ba}}kT\left\{\ln\left[\left(\frac{2\pi MkT}{h^2}\right)^{3/2}\frac{V_{\mathrm{Ba}}}{N_{\mathrm{Ba}}}\right]+1\right\}, \tag{3}$$

where M is the mass of a barium atom. The free energy of the crystal with $N_F - X$ singly ionized and X doubly ionized oxygen vacancies may be written

$$\begin{aligned}F_c = F_{\mathrm{cp}} + N_F E_F + N_F E_1 + XE_2 \\ - (N_F + X)kT\left\{\ln\left[2\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{V_c}{N_F+X}\right]+1\right\} \\ - kT\ln\left(\frac{(N+N_F)!}{N!\,X!\,(N_F-X)!}\right) - (N_F - X)T\Delta S_1 - XT\Delta S_2\,;\end{aligned} \tag{4}$$

F_{cp} is the free energy of the perfect crystal; E_F, E_1, and E_2 are, respectively, the formation energy of neutral oxygen vacancies, and the first and second ionization energies of these vacancies. The fifth term is the free energy of the electron gas in the conduction band, where m is the mass of the electron. The sixth term involves the entropy for mixing of the N oxygen ions, $N_F - X$ singly ionized vacancies, and X doubly ionized vacancies on $N + N_F$ available lattice sites. The last two terms involve the changes in thermal entropy of the crystal per vacancy ΔS_1 and ΔS_2 due to the introduction of singly and doubly ionized vacancies, respectively. Simplifying Eq. (4) using Sterling's approximation and applying Eqs. (1) and (2), and redefining N_{Ba}, N_F, N, and X as number densities, we obtain, respectively,

$$\frac{(N_F+X)(N_F-X)}{N_{\mathrm{Ba}}} = K_1 = 2N\left(\frac{m}{M}\right)^{3/2} e^{\Delta S_1/k}\, e^{-(E_F+E_1)/kT} \tag{5}$$

and

$$\frac{(N_F+X)X}{(N_F-X)} = K_2 = 2\left(\frac{2\pi mkT}{h^2}\right)^{3/2} e^{(\Delta S_2-\Delta S_1)/k}\, e^{-E_2/kT}\,. \tag{6}$$

There are two important limiting cases. For negligible second ionization, that is when $X \to 0$, Eq. (5) reduces to

$$N_F^2/N_{\mathrm{Ba}} = K_1 = C_1\, e^{-(E_F+E_1)/kT}\,. \tag{7}$$

For total second ionization, $X \to N_F$, the product of Eqs. (5) and (6) reduces to

$$N_F^3/N_{\mathrm{Ba}} = K_1K_2/4\,. \tag{8}$$

A log-log plot of N_F versus N_{Ba} for Eq. (7) will thus have a slope of $\frac{1}{2}$ and for Eq. (8) will have a slope of $\frac{1}{3}$.

A relationship valid for partial second ionization may be obtained by eliminating X between Eqs. (5) and (6). Thus

$$N_{\mathrm{Ba}} = \frac{4N_F^2 - \{[(N_F+K_2)^2 + 4N_FK_2]^{1/2} - N_F - K_2\}^2}{4K_1}\,. \tag{9}$$

A log-log plot of N_F versus N_{Ba} shows Eq. (9) to be concave up in the transition region of partial second ionization. For small but finite second ionization, that is for $K_2 \ll N_F$, a first-order approximation to Eq. (9) may be obtained as

$$(N_F^2 - K_2^2)/N_{\mathrm{Ba}} = K_1\,. \tag{10}$$

This, of course, reduces Eq. (7) with a slope of $\frac{1}{2}$ when $K_2 \to 0$. For low coloring densities and/or large second ionization, that is $N_F^2 \ll K_2$, Eq. (9) reduces to Eq. (8) with a slope of $\frac{1}{3}$.

III. EXPERIMENTAL

The crystals were grown from an open melt produced by a three-phase ac arc furnace using graphite electrodes. Spectroscopic analysis revealed that the principal impurities consisted of other alkaline earths. Amounts in ppm for representative crystals were as follows: 1700 Sr, 400 Ca, 5 Mg, 10 Fe, 1 Mn, and 1 Cu. The as-grown crystals were usually milky white (apparently due to microscopic bubbles) but could easily be cleared by annealing in vacuum at about 1440 °C for 2 h.

Initially, attempts were made to additively color these crystals using the previously described techniques that had been successfully used for MgO, SrO, and CaO.[7] This involved supporting the crystal in the top of a $\frac{3}{8}$-in.-diam, 6-in.-long tantalum bomb which contained a small amount of barium metal in the bottom. The bomb was then heated in a vacuum furnace with the top held at the desired temperature for coloration and the bottom at a temperature that would maintain the desired pressure of the barium vapor. However, the reproducibility of the resulting data was totally unacceptable. Using a special arrangement that would hold the bottom of the bombs at about 50 °C, which should have resulted in negligible coloration of the crystals, it was determined that not only were the crystals being colored due to a reaction with the tantalum but, because of the high vapor pressure of BaO, this BaO vapor was reacting with the tantalum and producing a significant Ba vapor pressure in the region of the crystal. These problems were eventually solved by completely enclosing the BaO crystal in a small box carved from two single crystals of MgO. The only significant openings in this box were two holes in the bottom directed into the main chamber of the bomb. The diameter of the bombs was also increased to $\frac{1}{2}$ in.

The barium vapor pressure P_{Ba} was determined from the temperature at the bottom of the bomb, T_{Ba}, using the practical vapor-pressure equations for barium developed by Nesmeyanov.[8] The density of Ba atoms at the crystal temperature was then determined using the ideal-gas law $N_{\mathrm{Ba}} = P_{\mathrm{Ba}}/kT_{\mathrm{BaO}}$.

All optical absorption data were taken at 77 °K

TABLE I. Coloration data for BaO. T_{BaO} was the temperature of crystal, T_{Ba} the temperature of barium metal, α_m the maximum optical absorption at 77 °K corrected for absorption of clear crystal, N_{Ba} the density of Ba atoms in the vapor, and N_F the resulting density of anion vacancies.

Crystal	T_{BaO} (°K)	T_{Ba} (°K)	α_m (cm^{-1})	N_{Ba} (10^{13} cm^{-3})	N_F (10^{17} cm^{-3})
*A*1	1423	802.6	5.97	0.508	0.454
*B*1	1423	883.4	33.27	5.10	2.53
*C*1	1423	985.2	63.93	52.2	4.87
*D*1	1423	1116	217.3	526	16.6
*E*1	1423	1163	386.4	1040	29.4
*A*2	1523	805.2	4.27	0.515	0.325
*B*2	1523	885.7	30.87	5.06	2.35
*C*2	1523	989.1	73.29	52.8	5.58
*D*2	1523	1121	260.4	531	19.8
*E*2	1523	1168	314.1	1050	23.9
*A*3	1623	807.1	3.84	0.514	0.293
*B*3	1623	888.1	32.15	5.04	2.54
*C*3	1623	992.1	80.17	52.6	6.10
*C*4	1623	992.1	89.96	52.6	6.85
*D*3	1623	1126	287.4	537	21.9
*E*3	1623	1172	338.0	1040	25.7
*A*4	1723	809.1	6.26	0.514	0.477
*B*4	1723	890.9	46.47	5.09	3.54
*B*5	1723	890.9	41.19	5.09	3.14
*C*4	1723	996.0	107.4	53.6	8.18
*D*4	1723	1129	268.4	526	20.4
*E*4	1723	1176	377.4	1040	28.7

since at higher temperatures the absorption band becomes complex due to the overlap of the *F* and F^+ bands.[6] The density of *F* centers was determined using Smakula's formula. Following Rose and Hensley,[6] the oscillator strength was taken to be $f = 0.8$, the index of refraction to be $n = 2.00$, and the absorption width at half-maximum to be $W_{1/2} = 0.85$ eV. Thus $N_F = 7.61 \times 10^{15} \alpha_m$, where α_m is the absorption coefficient at the peak corrected for the clear-crystal absorbance. This use of the original Lorentzian form of Smakula's equation represents a compromise since it has not yet been possible to accurately determine the exact shape of the high-energy side of the *F* band, primarily owing to the apparent pressure of an overlapping band of unknown origin at about 3.4 eV.[9] Any error involved is a simple scale factor for N_F which may be applied when better information of the band shape has been determined.

IV. RESULTS AND DISCUSSION

Although approximately 80 crystals were additively colored during the course of this investigation, only the data from the last 22 were considered valid. The earlier crystals were all expended in first recognizing and then solving the problem of irreproducible data due to extraneous coloration. The pertinent data for these 22 crystals were presented in Table I. The densities of anion vacancies N_F as a function of the densities of barium atoms in the vapor N_{Ba} for the four different coloring temperatures are shown in Fig. 1. The data for each temperature have been separated by factors of 10 since very little temperature dependence was observed.

The dashed lines (slope $\frac{1}{2}$) in Fig. 1 represent the equation

$$N_F^2 / N_{\mathrm{Ba}} = 1.98 \times 10^{22} e^{-0.42\ \mathrm{eV}/kT}, \tag{11}$$

which is the result of a least-squares fit of the data to the log of Eq. (7). The lowest Ba-vapor-pressure points labeled *A* were omitted from this least-squares fit for reasons to be discussed shortly. Dotted lines with slopes of $\frac{1}{3}$ and 1 are also shown in this figure for comparison. The small temperature dependence of these data may be noted by observing the intercepts of the dashed lines with the ordinate.

The data for the lowest Ba vapor pressure (points designated by *A*) were consistently observed to lie below the lines representing the rest of the data. An examination of Eq. (9) or (10) shows that any deviation from the slope-$\frac{1}{2}$ line should be concave up at low densities. This is a clear indication of a systematic error. One possible source of the error lies in the difficulty in making an accuracy

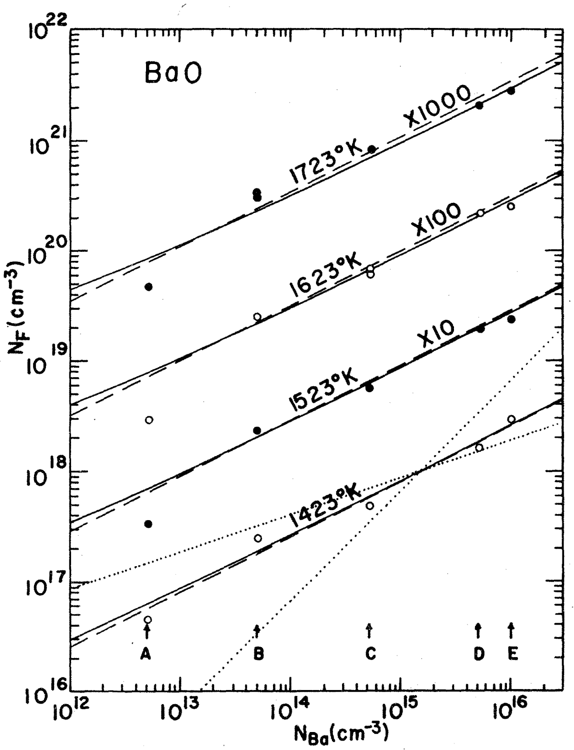

FIG. 1. Log-log plot of density of anion vacancies N_F versus density of barium atoms in vapor N_{Ba} for four different coloring temperatures. Least-squares fits of the data (excluding points *A*) to the log of Eq. (7) and the log of Eq. (10) are represented by the dashed lines and solid lines, respectively. Dotted lines with slopes of 1 and $\frac{1}{3}$ are shown for comparison.

determination of N_F at these low coloring densities. Not only is the induced absorbance much smaller than the absorbance of the clear crystal, but also an appreciable fraction of the vacancies will be in the F^+ state even at 77 °K,[6] both making it difficult to accurately estimate the induced absorbance.

Another possible explanation for the above anomaly involves the effect of electron traps at low coloring densities. However, these can be shown to have the opposite effect to that observed by considering the detailed balance involved in the additive coloring process. The rate of production of anion vacancies at the surface will be constant, independent of the degree of ionization of the resulting vacancies. However, the rate of reevaporation of the excess barium will depend on the simultaneous arrival at the same point on the surface of both a vacancy and the electrons to fill the vacancy. This bimolecular process is the reason for the equilibrium density of vacancies in the crystal being much higher than the density of barium atoms in the vapor even though the formation energy for neutral vacancies will be shown to be slightly endothermic. Any decrease in the density of electrons due to electron traps would result in a further decrease in the rate of reevaporation, which in turn would push the equilibrium concentration of vacancies even higher.

The most probable explanation of the above anomaly is that Nesmeyanov's vapor-pressure data were incorrect in this region. Nesmeyanov states[10] that "there are as yet no reliable data on the vapor pressure of solid barium, and that the best available data on liquid barium need to be rechecked." His "practical vapor-pressure equations" for barium were obtained "from the most reliable data, combined with thermodynamic functions." It is perhaps significant to note that the data for solid barium which Nesmeyanov rejected lies about a factor of 10 below his final curve. This would be more than enough to bring the points labeled *A* over to the dashed lines.

Careful study of Fig. 1 suggests that the points (excluding those labeled *A*) might be better fitted by a line with slope slightly less than $\frac{1}{2}$, thus suggesting the possibility of a small degree of second ionization. A computer program was written to make a least-squares fit of the data to the log of Eq. (10) for a sequence of values for the apparent second ionization energy (second ionization energy plus contribution due to change in thermal entropy) $E_2' = E_2 + (\Delta S_1 - \Delta S_2)T$ in the expression for K_2 [see Eq. (6)]. In this sequence of calculations, it was found that the standard deviation of the value for $E_F + E_1$, $\sigma(E_F + E_1)$, as well as the ratio of the standard deviation for C_1, $\sigma(C_1)/C_1$, both went through a shallow but definite minimum at a value for the apparent second ionization energy $E_2' = 1.07$. At this value for E_2', the least-squares fit gave a value of $E_F + E_1 = 0.15$ eV and $C_1 = 2.32 \times 10^{21}$. The solid curves in Fig. 1 represent a plot of Eq. (10) using these parameters.

In comparing the goodness of fit of the dashed lines with the solid curves in Fig. 1 it should be emphasized that the least-squares fit was made using the data for all four temperatures and was not a fit for each temperature separately. In addition to the reduction in the standard deviations for $E_F + E_1$ and C_1, the root mean square of the percent deviation of the data was reduced from 20% for the dashed lines to 12% for the solid lines (*A* points excluded). However, the improvement by either criterion cannot be regarded as overwhelmingly convincing. Additional data would, of course, be helpful but it is doubtful that the scatter could be reduced sufficiently to be conclusive.

It occurred to us that one test of the reliability of these results would be to make iterations of least-squares fits to subsets of the present data in which portions had been systematically deleted. The results of such calculations are summarized in Table II. Only when all of the data are included, as in the first line of Table II, do the calculations fail to indicate the presence of second ionization. However, we have already presented reasons for excluding the points labeled *A*. The second line of Table II gives the parameters used in plotting the solid curves in Fig. 1. The next four lines show the results of deleting the points labeled *B* through *E* in addition to *A*. These all give surprisingly similar results. The bottom five lines in Table II show the results of artificially fixing E_2' large enough to ensure negligible second ionization. The first of this set of lines gives the parameters used for Eq. (11) and in plotting the dashed lines in Fig. 1. It will be noted that the standard deviations for these last five lines are greater than for the cor-

TABLE II. Parameters resulting from least-squares fits of selected portions of the data to Eq. (10). The first six lines are for the values of $E_2' = E_2 + (\Delta S_1 - \Delta S_2)T$, which result in minimum values for the standard deviations $\sigma(E_F + E_1)$ and $\sigma(C_1)/C_1$. The last five lines are for E_2' fixed.

Points omitted	E_2' (eV)	E_F+E_1 (eV)	$\sigma(E_F+E_1)$ (eV)	C_1 (cm^{-3})	$\sigma(C_1)/C_1$
None	>2.0	0.37	0.25	1.09×10^{22}	7.22
A	1.07	0.15	0.13	2.32×10^{21}	5.30
A, B	0.98	0.21	0.11	3.33×10^{21}	9.89
A, C	1.06	−0.02	0.14	6.48×10^{20}	9.68
A, D	1.07	0.11	0.16	1.68×10^{21}	8.55
A, E	1.07	0.20	0.15	3.32×10^{21}	8.99
A	set >2	0.42	0.18	1.98×10^{22}	6.57
A, B	set >2	0.33	0.12	8.25×10^{21}	10.39
A, C	set >2	0.34	0.23	1.18×10^{22}	13.51
A, D	set >2	0.44	0.23	2.40×10^{22}	11.73
A, E	set >2	0.53	0.21	4.83×10^{22}	11.30

responding lines above. These bottom five lines represent, respectively, the starting points for the iterations with respect to E_2' while the preceding five lines represent the points where $\sigma(E_F + E_1)$ and $\sigma(C_1)/C_1$ were at a minimum.

From his paper alone, it was difficult to determine why Timmer's results should differ from ours. Although he used Rudberg and Lempert's[11] barium-vapor-pressure curve, replotting his data using Nesmeyanov's curve shifted his data points to the right by about a factor of 10, but resulted in only an insignificant increase in slope. However, by referring to his thesis,[12] we learned that not only were his optical-absorption measurements made at room temperature, but also he measured his absorption maxima from the bottom of the minimum produced between the infrared tail (now shown to be due to free carriers[6]) and the F-center absorption band. At room temperature the absorption band will be a mixture of F and F^+ bands (peaking at 2.3 and 2.0 eV, respectively[6]). Also, both the ratio of the densities of the F and F^+ centers and the magnitude of the infrared tail will be functions of the density of coloration. These effects are strong enough to easily account for the observed differences between Timmer's results and ours. Timmer did make a blank coloring run (no barium vapor) so it is doubtful that with his bomb configuration he was bothered by extraneous coloration.

V. CONCLUSIONS

In summarizing the results of this investigation it is important to emphasize the extent to which these results are dependent on the accuracy of Nesmeyanov's vapor-pressure curve for barium. We have already pointed out that the anomalous deviation of the lowest density points (labeled A) in Fig. 1 indicates that the vapor-pressure curve is probably too high in this region. While we have less reason to question the upper portion of the vapor-pressure curve, it too should be regarded with caution. From the point of view of predicting the density of coloration of barium oxide there are essentially no difficulties as the procedure may be regarded as purely empirical. However, in determining the parameters in the theory, or indeed, determining whether in fact second ionization of the anion vacancies actually occurs in the additive coloring process, reliable vapor-pressure data are essential. If at some future date, more definitive results for the vapor pressure of barium become available, the data provided in Table I will make it possible to recalculate the results obtained here.

It is a conclusion of this investigation that Eq. (11) is a good representation of the additive coloring process in barium oxide. Excluding the lowest density points (labeled A in Fig. 1), the root mean square of the percent deviation of the data from Eq. (11) is 20%. At lower densities, the uncertainties will be somewhat larger, primarily because of the uncertainties in the barium-vapor-pressure curve. In general, the departure from Eq. (11) arising from second ionization of the anion vacancies will be less than the above experimental uncertainties.

It is also tentatively concluded that there is a significant fraction of the anion vacancies that are doubly ionized at the coloring temperature. The root mean square of the percent deviation of the data is reduced to 12% when Eq. (10) is used compared to 20% when Eq. (11) is used (A points excluded). From the parameters resulting from the least-squares fit to the data (line 2 of Table II) we observe that the apparent second ionization energy has a value $E_2' = E_2 + (\Delta S_1 - \Delta S_2)T = 1.07$ eV. Using Rose and Hensley's[6] value for the first ionization energy, $E_1 = 0.1$ eV, the formation energy for anion vacancies in barium oxide is $E_F = 0.15 - E_1 = 0.05$ eV. The corresponding formation energies for MgO,[2] CaO,[3] and SrO,[4] are, respectively, 1.53, 0.234, and −1.1 eV. Thus it is seen that the trend from endothermic to exothermic reactions as one proceeds from the light to heavy oxides is reversed by BaO. However, it should be noted that the determination of the formation energy E_F is strongly influenced by the inclusion of second ionization in the theory. If second ionization were neglected, as in Eq. (11), the formation energy would be interpreted as being $E_F = 0.42 - E_1 = 0.32$ eV. Thus the possibility exists that a redetermination of the barium-vapor-pressure curve could significantly alter these conclusions.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Benny H. Rose for assistance during the early phases of this investigation and Dr. David L. Cowan for helpful discussions.

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†Work supported in part by National Science Foundation.

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