

The Electrical Conductivity of Single Crystals of Ag_2HgI_4

K. W. BROWALL AND J. S. KASPER

General Electric Research and Development, Schenectady, New York

Received October 1, 1974

Electrical conductivity measurements are reported for single crystal samples of Ag_2HgI_4 in the temperature range between -17°C and 72°C . The results are interpreted in terms of two distinct regions of linear log conductivity versus reciprocal temperature behavior for $\beta\text{-Ag}_2\text{HgI}_4$, a phase transition region, and an $\alpha\text{-Ag}_2\text{HgI}_4$ region. The data reaffirm the anomalously high pre-exponential and activation energy terms in the conductivity equation for $\alpha\text{-Ag}_2\text{HgI}_4$ as compared with other AgI-type conductors. Thermo-emf measurements on polycrystalline Ag_2HgI_4 samples are also reported.

Introduction

The high ionic conductivity of Ag_2HgI_4 is well known. The first report on the electrical conductivity of polycrystalline Ag_2HgI_4 samples by Ketelaar (1) in 1938 revealed a sharp discontinuity in the log conductivity (σ) versus reciprocal temperature curve at 50.7°C , with $\sigma \sim 10^{-3}\Omega^{-1}\text{cm}^{-1}$ just above the 50.7° transition temperature. Several reinvestigations of the solid state conductivity as a function of temperature (2, 3), temperature and pressure (4), and pressure (5) have been made since then. Although the various reports are in general agreement with respect to the conductivity magnitude, there exists considerable variance in the values of the σ_0 and E_a terms in the equation, $\sigma = \sigma_0 \exp(-E_a/kT)$, where E_a is the thermal activation energy for conduction, for both the low temperature ($\beta\text{-Ag}_2\text{HgI}_4$) and high temperature ($\alpha\text{-Ag}_2\text{HgI}_4$) modifications. In addition, the results have shown varying but generally large degrees of conductivity hysteresis as a function of temperature. All previous studies have been restricted to polycrystalline samples, with some apparent dependence of the conduction properties on the method of sample preparation and the sample history (3).

Specific interest has been focused on Ag_2HgI_4 among the highly conducting AgI-based "solid electrolytes" because of the recent availability of single crystals (6) and its anomalous characteristics relative to other members of this class of compounds. For example, $\alpha\text{-Ag}_2\text{HgI}_4$ exhibits a pre-exponential (σ_0) term two orders of magnitude larger and an activation energy (E_a) three times larger than other AgI-based conductors (7). The present study, for the first time, includes ac and dc conductivity measurements of single-crystal samples as a function of temperature. Previous papers in this series (6, 8) have dealt with the structure and phase transformation properties of α and $\beta\text{-Ag}_2\text{HgI}_4$.

Experimental

Preparation and Stability of Ag_2HgI_4

The preparation of Ag_2HgI_4 single crystals has been described previously (6, 9). The crystals that were selected for conductivity measurements were typically optically clear well-formed yellow-needles. Crystals ~ 0.2 mm long and with either $\sim 0.05 \times 0.02$ mm rectangular cross section or ~ 0.06 mm sided triangular cross section were measured. The same crystal instability problems as had been

encountered during X ray investigation (6, 8) were observed in the conductivity specimens. Again, only the most perfect crystals were used, although this alone did not guarantee a stable specimen throughout the conductivity measurement. Powdered Ag_2HgI_4 samples were made by mixing stoichiometric amounts of aqueous K_2HgI_4 and AgNO_3 , filtering, and washing the precipitate thoroughly with distilled water.

Electrical Conductivity Measurements

Single crystals of Ag_2HgI_4 were wired for two-probe electrical conductivity measurements along the needle axis ([110] crystal direction). Four-probe measurements were not possible due to the crystal size and fragility. Electrical contact to the sample was made with 0.5 mil gold-coated tungsten wire attached with aquadag electrodes. Silver paint electrodes were tried also, but this caused some discoloration of the crystal. Measurements were carried out as a function of temperature in a specially designed apparatus either *in vacuo* at pressures $<10^{-5}$ Torr or in a dry N_2 atmosphere. Samples were mounted on interchangeable electrically insulating textolite sheets equipped with temperature-controlled heat-sink wire connections, and then were attached to a temperature-controlled massive copper block. Two thermocouples were used to monitor the working temperature range of -17 to $+72^\circ\text{C}$. Heating rates generally ranged from 5° to $10^\circ/\text{hr}$.

Both ac and dc conductivity measurements were carried out. A Wayne Kerr Model B224 conductance bridge with 1592 Hz internal frequency was used for the ac measurements; an auxiliary frequency generator was used for several ac measurements at 800 and 6000 Hz. The dc measurements were made using a Keithley Model 610C electrometer having an input impedance $>10^{14} \Omega$.

The conductivity was determined from the relationship, $\sigma = l/(AR)$, where σ = conductivity, R = measured sample resistance, l = sample length, and A = sample cross-sectional area (i.e., electrode area). The limiting factor in determining absolute conductivities was

considered to be error in measuring the value of l/A for such small crystals. A linear $\log \sigma$ versus $1/T$ relationship was found in each case, in accordance with the equation

$$\sigma = \sigma_0 \exp(-E_a/kT).$$

A least-squares analysis of the data yielded values of σ_0 and E_a .

Thermo-emf Measurements

A polycrystalline pressed pellet sample of Ag_2HgI_4 was sandwiched between two massive copper blocks, while temperature differentials of between 2 and 20°C were applied as a function of temperature, as determined by absolute and differential thermocouples attached to the copper blocks. The entire assembly was mounted in a shielded cage to avoid spurious voltages. The resulting voltage was measured using a Keithley 610C electrometer. The Seebeck coefficient was determined from the relationship $\varepsilon = |V/\Delta T|$, where V is the observed voltage and ΔT is the temperature differential.

Results

The results of the ac and dc electrical conductivity measurements on single crystals of Ag_2HgI_4 are summarized in Table I. Fig. 1 shows a plot of $\log \sigma$ versus $1/T$, based on the averaged results, while Fig. 2 shows the same plot for a particular set of typical ac measurements. The results may be considered in terms of three distinct temperature regions: two low temperature regions (β - Ag_2HgI_4), one for $T < 16^\circ\text{C}$, and another for $16^\circ\text{C} < T < 48^\circ$, and a high temperature region (α - Ag_2HgI_4), where $T > 52^\circ\text{C}$. In each case, the log of the conductivity increases linearly as reciprocal temperature decreases. A sharp jump in the conductivity is observed in the vicinity of 48 – 52°C , associated with the $\beta \rightarrow \alpha$ phase change.

Measurements were restricted to dc at temperatures $<36^\circ\text{C}$ and to ac at temperatures $>23^\circ\text{C}$ on account of the high sample resistance at low temperatures and excessive dc polarization at high temperatures. Several of the ac measurements were made as a function

TABLE I
SINGLE CRYSTAL CONDUCTIVITY^a DATA FOR Ag₂HgI₄

Temperature range	Number of crystals measured	ac ^b /dc	σ_0	E^a (ev)
-17° → +16°	3	dc	2.2×10^3	0.58 ± 0.03
16° → 36°	3	dc	1.3×10^6	0.74 ± 0.01
23° → 48°	6	ac	2.6×10^7	0.81 ± 0.04
51° → 72°c	2	ac	1.6×10^2	0.33 ± 0.05

^a Along needle axis.

^b At 1592 Hz.

^c Measurements taken with temperature increasing.

of frequency, at 800, 1592, and 6000 Hz, but below 48° (β -Ag₂HgI₄), no frequency dependence of the conductivity was detected. Above 52°C (α -Ag₂HgI₄), measurements of the frequency dependence on one sample indicated that the conductivity increased in the order $\sigma_{800 \text{ Hz}} < \sigma_{1592 \text{ Hz}} = \sigma_{6000 \text{ Hz}}$. At 60°C, for example, $\sigma_{800 \text{ Hz}} = 7.3 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ and $\sigma_{1592 \text{ Hz}} = \sigma_{6000 \text{ Hz}} = 1.2 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$. In the

limited region where both ac and dc measurements were possible (23–36°C) the dc conductivities were consistently lower than the ac (1592 Hz) values for the same sample, but only by about 20%. Both the activation energy for conduction and the σ_0 term are slightly lower for dc than ac (Table I).

The behavior of the conductivity in the region of the $\beta \rightarrow \alpha$ and $\alpha \rightarrow \beta$ phase trans-

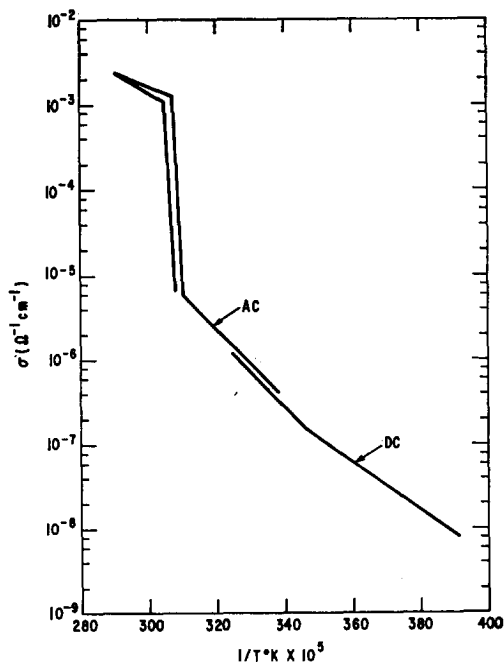


FIG. 1. Results of electrical conductivity measurements on Ag₂HgI₄ single crystals as a function of temperature.

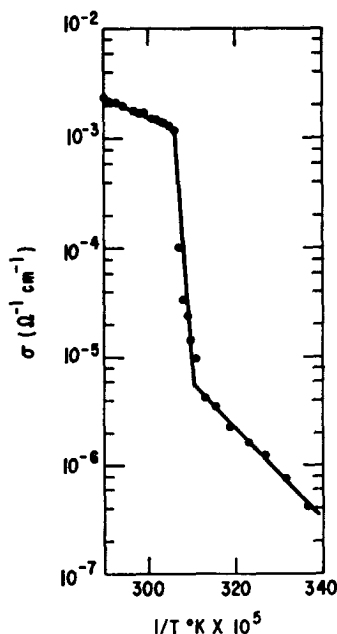


FIG. 2. Typical conductivity run data for a particular Ag₂HgI₄ crystal.

formation was also investigated. Paralleling the problems previously encountered during our X ray studies, many crystals behaved anomalously when heated. Even though the conductivity behavior of a particular crystal below 50°C might be in agreement with "good" crystals, decomposition of the crystal often occurred just before, during, or just after the phase transformation. For example, the conductivity would begin to increase sharply as the transition temperature was reached and then sharply decrease (to an even lower value than expected for the $\beta\text{-Ag}_2\text{HgI}_4$ modification) before ever reaching the expected $\alpha\text{-Ag}_2\text{HgI}_4$ conductivity. The details of the decomposition behavior were by no means consistent from sample to sample, however. On the other hand, for the "well-behaved" crystals, very little hysteresis was noted in the transition behavior. In these cases, the conductivity reversibly shifted by several orders of magnitude, with the transition midpoint at 51.3°C for increasing temperature and 53.1°C for decreasing temperature.

The results of thermoelectric power measurements on polycrystalline Ag_2HgI_4 are shown in Fig. 3. Although these results are considered to be only semiquantitative and limited in temperature range, $\alpha\text{-Ag}_2\text{HgI}_4$ obeys the equation $\varepsilon = 193 - (3.22 \times 10^5)/T$, and $\beta\text{-Ag}_2\text{HgI}_4$ obeys the equation $\varepsilon = 1520 - (7.6 \times 10^5)/T$, where ε is the thermoelectric power in $\mu\text{V deg}^{-1}$ and T is absolute temperature. The sign of the Seebeck coefficient, in both cases, is negative.

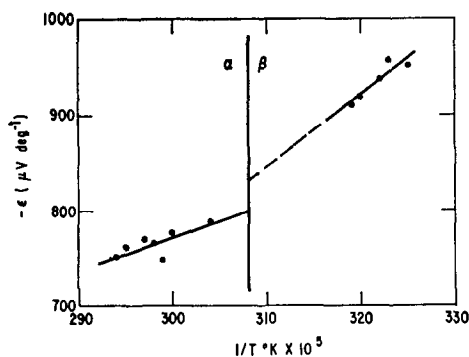


FIG. 3. Results of thermo-emf measurements on polycrystalline Ag_2HgI_4 .

Discussion

The results of electrical conductivity measurements on single crystals of Ag_2HgI_4 are broadly similar to previously reported results for polycrystalline specimens. In each case, regions of linear $\ln \sigma$ versus $1/T$ behavior are separated by a discontinuous jump in the conductivity coincident with the $\beta \rightleftharpoons \alpha$ phase transition. Although crystal quality was found to be extremely critical, poor quality crystals were readily detected during the conductivity measurements by their anomalous and irreproducible behavior. Postrun examination of these crystals usually revealed that the crystal had lightened in color, possibly indicating loss of HgI_2 . These observations on single crystals point out a possible pitfall of previous studies of polycrystalline samples, where it is possible for partial decomposition of the sample to occur without obvious visual or conductivity detection. Indeed, it has been noted that the conductivity behavior of polycrystalline samples is dependent on the pressure at which pellets are pressed, the sample history, and the time-schedule (3). In contrast, the variations observed among crystals were relatively small, so that standard deviations for the thermal activation energy for conduction range from ± 0.01 ev to ± 0.05 ev (Table I). Determination of the very sensitive σ_0 term is subject to greater errors because of the difficulties associated with measuring the crystal dimensions, but these errors should be reduced somewhat by averaging the σ_0 values.

Least squares analysis of the single crystal results revealed that the conductivity of $\beta\text{-Ag}_2\text{HgI}_4$ is clearly divided into two distinct segments of linear $\ln \sigma$ versus $1/T$ behavior, one between 48°C and 16°C , and one below 16°C . This result may explain the apparent large discrepancies among the earlier studies, since Suchow and Pond (2) did not report measurements below $\sim 10^\circ\text{C}$ and Neubert and Nichols (3) found nonlinear behavior above 20°C . Our results below 16° are in general agreement with the Neubert and Nichols study (3), both with respect to σ_0 ($2.2 \times 10^3 \Omega^{-1}$ versus $5.9 \times 10^2 \Omega^{-1} \text{cm}^{-1}$) and E_a (0.58 ev versus 0.52 ev), while our results between 16° and the transition temperature are in fair

agreement with the Suchow and Pond (2) results [$\sigma_0 = 2.6 \times 10^7 \Omega^{-1} \text{ cm}^{-1}$ (ac) or $1.3 \times 10^6 \Omega^{-1} \text{ cm}^{-1}$ (dc) versus $1.4 \times 10^6 \Omega^{-1} \text{ cm}^{-1}$ and $E_a = 0.81 \text{ eV}$ (ac) or 0.74 eV (dc) versus 0.71 eV]. These results and comparisons are summarized in Table II. The nonlinear $\ln \sigma$ versus $1/T$ behavior that Neubert and Nichols observed between 20°C and the transition temperature, and which has been observed to some extent on other studies on polycrystalline samples just below the $\beta \rightarrow \alpha$ transition temperature, is not observed in single-crystal samples until $T \geq 48^\circ\text{C}$, the onset of the phase transition. It is conceivable that such non-linearity is the result of partial decomposition in the polycrystalline sample.

The ac-conductivity in the $\beta\text{-Ag}_2\text{HgI}_4$ region ($48^\circ > T > 23^\circ\text{C}$) is not frequency dependent, within experimental error, in the range from 800–6000 Hz. However, the dc-conductivity in the same region has a slightly lower σ_0 ($1.3 \times 10^6 \Omega^{-1} \text{ cm}^{-1}$ versus $2.6 \times 10^7 \Omega^{-1} \text{ cm}^{-1}$) and slightly lower activation energy (0.74 eV versus 0.81 eV). Below 36° no dc polarization of the crystals was observed, but polarization became prominent as the transition temperature was approached, and became excessive for attempted dc measurements on $\alpha\text{-Ag}_2\text{HgI}_4$. These results would be consistent with the interpretations by Weil and Lawson (4) and recently by Webb (5) that $\beta\text{-Ag}_2\text{HgI}_4$ is primarily an electronic conductor, while $\alpha\text{-Ag}_2\text{HgI}_4$ is primarily an ionic conductor.

The phase transformation for single crystals was found to be remarkably sharp and to show far less hysteresis than had previously been reported for polycrystalline samples. Despite the fact that relatively rapid heating rates (up to $10^\circ/\text{hr}$) were employed, hysteresis for the transition was only about 2°C , and the transition occurred over only a 3° range. Possibly hysteresis could have been further reduced by slower heating rates. Hysteresis of $3\text{--}7^\circ$ and 8° was noted by Neubert and Nichols (3) and by Suchow and Pond (2), respectively. A comparison of the transition temperatures is included in Table II. The single crystal value of 51.3° (increasing temperature) is well within the range of polycrystalline specimen results.

For $\alpha\text{-Ag}_2\text{HgI}_4$, the Seebeck coefficient is

TABLE II
COMPARISON OF CONDUCTIVITY DATA

Reference	$\alpha\text{-Ag}_2\text{HgI}_4$			$\beta\text{-Ag}_2\text{HgI}_4$			$T_{\beta \rightarrow \alpha}$
	$\sigma_0 (\Omega^{-1} \text{ cm}^{-1})$	$E_a (\text{eV})$	$\sigma_0 (\Omega^{-1} \text{ cm}^{-1})$	$E_a (\text{eV})$	$\sigma_0 (\Omega^{-1} \text{ cm}^{-1})$	$E_a (\text{eV})$	
(1) ^a	4×10^2	0.37	—	—	—	—	50.7°
(2) ^a	7.5×10^3	0.44	$1.4 \times 10^6, T > 10^\circ$	—	—	—	50.0°
(3) ^a	3.64×10^{-1}	0.16	$9.9 \times 10^4, T > 22^\circ$	—	$5.9 \times 10^2, T < 20^\circ$	$0.52, T < 20^\circ$	52°
(4) ^a	—	0.52	—	—	—	—	—
This work ^b	1.6×10^2	0.33	$1.3 \times 10^6, T > 16^\circ$ $2.6 \times 10^7, T > 23^\circ$	$0.74, T > 16^\circ$ $0.81, T > 23^\circ$	$2.2 \times 10^3, T < 16^\circ$	$0.58, T < 16^\circ$	51.3°

^a Polycrystalline sample.

^b Single crystal sample.

^c dc value.

$[+193 - (3.22 \times 10^5/T)] \mu\text{V deg}^{-1}$, quite close to the value reported by Magistris et al. (10), $[+278 - (4.02 \times 10^5/T) \mu\text{V deg}^{-1}$. The thermoelectric power is higher for $\beta\text{-Ag}_2\text{HgI}_4$, $[+1520 - (7.64 \times 10^5/T)] \mu\text{V deg}^{-1}$, in direct contrast to the lower, temperature-independent value reported by Magistris et al. (10). Although the sign of the Seebeck coefficient is typically associated with the sign of the charge carrier, this correlation holds true only for the simplest of systems. Previous work (10, 11) on silver ion conductors has shown that the Seebeck coefficient is always negative, in agreement with our results. A quantitative evaluation of the significances of thermo-emf data for solid ionic conductors is not available.

The ac measurements on the high temperature modification (α) are of special interest because of the unusual status of $\alpha\text{-Ag}_2\text{HgI}_4$, among Ag-containing ionic conductors, with respect to the large values of both σ_0 and the activation energy that have been reported. This feature has received attention by Wiedersich and Geller (12) and Rice and Roth (13) and is apparent in the compilation of Armstrong et al. (7). The value of the activation energy (E_a) used by all these authors is 0.40 eV [presumably the original Ketelaar (1) result, which exactly is 0.37 eV], a value that is considerably larger than that typical of the good ionic conductors, i.e., 0.1 eV. The result from our single crystal data (0.33 eV) agrees best with that of Ketelaar and substantiates the atypical nature of $\alpha\text{-Ag}_2\text{HgI}_4$ in this respect.

The pre-exponential term of the conductivity expression, or quantities derived from it, has been consistently reported (for the α -form) as larger by about two orders of magnitude than the typical value for a good conductor. Our result of $\sigma_0 = 160 \Omega^{-1} \text{cm}^{-1}$ is somewhat lower than that of Ketelaar ($\sigma_0 = 400 \Omega^{-1} \text{cm}^{-1}$) but is still in better agreement with it than various values obtained from other polycrystalline studies (see Table II). We conclude that σ_0 of $\alpha\text{-Ag}_2\text{HgI}_4$ is still larger than the typical σ_0 of a good conductor (at equal temperatures) but by only one order of magnitude (160 versus 5 to $10 \Omega^{-1} \text{cm}^{-1}$).

Accepting our single crystal determinations of σ_0 and E_a as the most reliable, $\alpha\text{-Ag}_2\text{HgI}_4$ is still to be considered as abnormal in relation to the other good ionic conductors and there remains the problem of understanding the reasons for the abnormality. There is no available theory that allows quantitative evaluation of the conductivity parameters from first principles. Of the various suggestions for the conductivity behavior of $\alpha\text{-Ag}_2\text{HgI}_4$ we find those of Wiedersich and Geller (12), based on structural considerations, to be reasonable and most acceptable. Wiedersich and Geller have pointed out that the face-centered anion arrangement of $\alpha\text{-Ag}_2\text{HgI}_4$ does not allow direct passage of cations from one tetrahedral interstice to another, as is the case for $\alpha\text{-AgI}$, RbAg_4I_5 and most of the other good conductors. They suggest that the most probable path is via the unoccupied octahedral interstices. Thus, creation of interstitial ions in octahedral sites is required for cation migration with an activation energy similar to that found for the creation of defects, interstitial or vacancy, in the classic examples of alkali and normal silver halides. The E_a value of 0.33 eV for $\alpha\text{-Ag}_2\text{HgI}_4$ is reasonable for such a process.

Our previous structural (8) study of $\alpha\text{-Ag}_2\text{HgI}_4$ adds further support to those notions. We found that indeed only the one set of tetrahedral interstices of the zincblende structure are occupied by cations, with no appreciable occupancy of any other interstices. Furthermore, the large anharmonic vibrations of the cations are in the direction of the octahedral interstices.

Regarding the large value of σ_0 for $\alpha\text{-Ag}_2\text{HgI}_4$, we note that this may be attributed to the high concentration of carriers in a conductivity mechanism that is otherwise the same as the conventional one for defect migration. Consider the general expression for conductivity, $\sigma = nZeV$, where n is the concentration of charge carriers, Ze is their charge, and V is their mobility. If n for $\alpha\text{-Ag}_2\text{HgI}_4$ is taken as $0.77 \times 10^{22} \text{cm}^{-3}$, i.e., the total concentration of Ag^+ , then $V = 2.2 \times 10^{-6} \text{cm}^2/\text{V sec}$. This number is about two orders of magnitude smaller than characteristic numbers for mobilities of Ag in AgI,

Ag_4RbI_5 , and Ag_2Te , but is more typical of defect mobilities in the poor conductors [see Table III of Armstrong et al. (7)]. If, further, the mobility is considered as $V = A/T \exp(-\Delta H_m/RT)$ in the notation of Armstrong et al., both A and $-\Delta H_m$, the heat of activation for movement of the mobile species, assume values for $\alpha\text{-Ag}_2\text{HgI}_4$ similar to those for the poor conductors including AgCl and AgBr . Of course, it is possible to ascribe higher mobilities to Ag^+ and consider the concentration of Ag^+ to be less than the total concentration, but it would seem more advantageous to consider the mechanism of conductivity in $\alpha\text{-Ag}_2\text{HgI}_4$ to be similar to the conventional defect mechanism and differing only by virtue of the high concentration of charge carriers.

Attention has been given to $\alpha\text{-Ag}_2\text{HgI}_4$ by Rice and Roth (13) in their free ion theory of conductivity. The large value of the pre-exponential results in a large value of the parameter l_0 , the mean free path of the free ion, 96 Å in their tabulation. Our value of σ_0 of $160 \Omega^{-1} \text{cm}^{-1}$ corresponds to $l_0 = 14.3$ Å. Accepting this as still a larger value than the l_0 for the other good conductors, it does not seem appropriate to consider l_0 in a literal sense as implying any extended uninterrupted paths for the migration process. $\alpha\text{-Ag}_2\text{HgI}_4$, despite its anomalous conductivity characteristics, does not appear to be a good example in support of the free ion theory of conductivity.

Acknowledgement

This research was supported, in part, by the Air Force Office of Scientific Research under AFOSR Contract F44620-72-0041C.

References

1. J. A. A. KETELAAR, *Trans. Faraday Soc.* **34**, 874 (1938).
2. L. SUCHOW AND G. R. POND, *J. Amer. Chem. Soc.* **75**, 5242 (1953).
3. T. J. NEUBERT AND G. M. NICHOLS, *J. Amer. Chem. Soc.* **80**, 2619 (1958).
4. R. WEIL AND A. W. LAWSON, *J. Chem. Phys.* **41**, 832 (1964).
5. A. W. WEBB, *J. Phys. Chem. Solids* **34**, 501 (1973).
6. K. W. BROWALL, J. S. KASPER, AND H. WIEDEMEIER, *J. Solid State Chem.* **10**, 20 (1974).
7. R. D. ARMSTRONG, R. S. BULMER, AND T. DICKINSON, *J. Solid State Chem.* **8**, 219 (1973).
8. J. S. KASPER AND K. W. BROWALL, *J. Solid State Chem.*, **13**, 49 (1975).
9. C. E. OLSON AND P. M. HARRIS, Air Force Report AFOSR-TN-59-756.
10. A. MAGISTRIS, E. PEZZATI, AND C. SINISTRÌ, *Z. Naturforsch* **27a**, 1379 (1972).
11. T. TAKAHASHI, O. YAMAMOTO, AND E. NOMURA, *Denki Kagaku* **38**, 360 (1970).
12. H. WIEDERSICH AND S. GELLER, in "The Chemistry of Extended Defects in Non-metallic Solids" (L. Eyring and M. O'Keefe, Eds.), p. 629, North-Holland, Amsterdam (1970).
13. M. J. RICE AND W. L. ROTH, *J. Solid State Chem.* **4**, 294 (1972).