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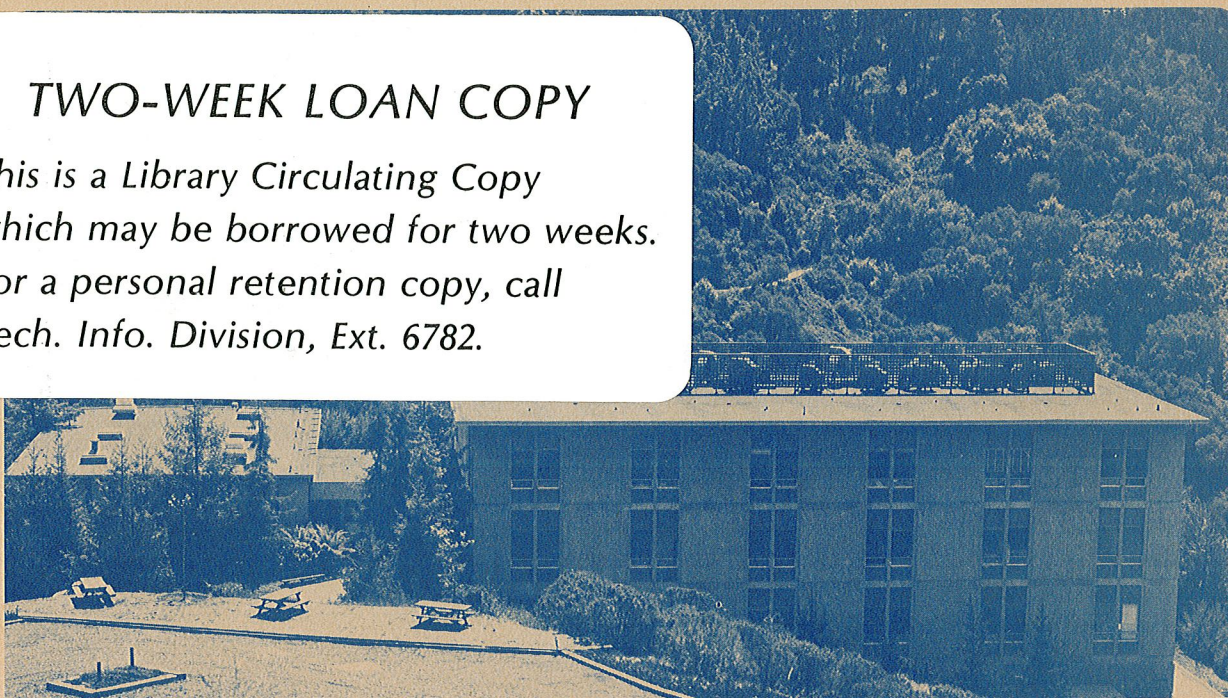
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ELECTRONIC CERAMICS IN HIGH TEMPERATURE ENVIRONMENTS*

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ABSTRACT

Simple thermodynamic means are described for understanding and predicting the influence of temperature changes in various environments on electronic properties of ceramics. Thermal gradients, thermal cycling and vacuum annealing are discussed, as well as the variations of activities and solubilities with temperature.

*Presented as the introductory address of the session on Electronic Ceramics in Severe Environments at the 33rd Pacific Coast Meeting, San Francisco, October 28, 1980.

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In high temperature environments electronic ceramics are likely to undergo property changes and chemical reactions that are unexpected from room temperature studies. The purpose of this communication is to illustrate the nature of some effects of high temperatures and to outline in simple terms why they occur and how they can sometimes be predicted. Some of our illustrative examples are not from electronic systems, but the behavior illustrated can be expected in electronic systems as well.

The desired levels of electrical defects in semiconducting materials are usually set by additions of dopants or impurities, that is, they are "extrinsically" set. When these extrinsic semiconductors are heated to high enough temperatures their conductivity eventually becomes controlled by the intrinsic defect concentrations. This well known fact can be illustrated by the example of germanium (Fig. 1)¹. Germanium specimens which contain a $10^{23}/\text{m}^3$ concentration of either an n or p type dopant become intrinsic semiconductors when heated above 600°K. If the dopant level is decreased to $10^{19}/\text{m}^3$ the germanium becomes an intrinsic semiconductor at just over 300°K.

In an intrinsic semiconductor the concentration of current carriers increases in an exponential fashion according to the expression,

$$pn = n_i^2 = N_C N_V \exp[(\epsilon_C - \epsilon_V)/kT] .$$

*Keynote address

- p, n : Concentrations of positive holes and electrons, respectively, which are current carriers.
- n_i : Intrinsic current carrier concentration.
- N_C, N_V : Concentration of states in the conduction and valence bands, respectively.
- ϵ_C, ϵ_V : Energies of the bottom of the conduction band and the top of the valence band, respectively.

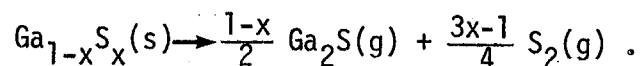
For extrinsic semiconductors the concentration of carriers varies with temperature in a more complex manner, as indicated schematically in Fig. 2, which is for a semiconductor doped with both acceptors of concentration N_A and donors of concentration N_D , with $N_D \gg N_A^2$. Despite the complexity, it can be seen that the variation of electron carrier concentration with temperature is much smaller in the extrinsic regions (a), (b) and (c) than in the intrinsic region (d). This is a result of the fact that the energy required to ionize a donor (or acceptor) atom is much less than the energy difference between the conduction and valence bands.

Since the concentration of electrons and holes are essentially the same in an intrinsic semiconductor, pn junctions cease to operate as such when a semiconductor is in the intrinsic region. Other factors being equal, for semiconductor operation at high temperatures one would prefer substances that have the largest possible intrinsic band gaps so that the extrinsic range can be extended to high temperatures.

In compound semiconductors the concentration of electrical defects is a function not only of the doping agents added but also of the metal to non-metal ratio in the host lattice. Data from J. Bloem illustrate this point³.

For our present purposes it is instructive to consider the data that he collected for pure, undoped PbS (Fig. 3). The data show that if PbS is brought to equilibrium with an S₂ pressure of 0.01 atm. at 1000°K the PbS will be a p-type semiconductor while if it is brought to equilibrium with the same pressure of S₂ at 1200°K the PbS will be an n-type semiconductor. The principal carrier in this compound is a function of temperature at constant S₂ pressure because at constant S₂ pressure an increase in temperature shifts the composition of the solid PbS phase toward a higher lead to sulfur ratio. This shift in composition with temperature and its consequent change in electrical properties reflect the fact that in a multi-component phase the partial pressures of the individual components, or, in other terms, their thermodynamic activities, at a given composition have different temperature dependencies.

It is worth noting that existence of different temperature dependencies of activities of components in a solid phase can be used in a constructive way to fine tune the composition and therefore the electrical properties. The composition of a congruently vaporizing solid can be shifted by heating the solid to different high temperatures and partially vaporizing it, even though the composition change may be too small to measure readily. The principle is illustrated by the experiments of Roberts and Searcy⁴ using gallium sulfide, which vaporizes according to the reaction,



In this equation x is a function of temperature. For the temperature range 1040° to 1300°K the change in x amounts to about 0.4 mole percent

sulfur, which is too small a variation to measure by ordinary analytic means. Fig. 4 illustrates how the variation of x with temperature could be determined by mass spectrometry. Steady state vaporization is first established at any temperature T_1 . Intensities of the Ga_2S^+ and S_2^+ ions are then in a constant ratio to each other of about 1:1, the exact value of which depends on the ionization cross-sections of the gaseous molecules and on various instrumental factors. When the temperature is then changed to a different temperature T_2 , the ion ratio is shifted because the partial pressure of S_2 varies more strongly with the temperature than does the partial pressure of Ga_2S . If, for example, T_2 is greater than T_1 , the sample then loses S_2 preferentially until the composition has been shifted to the new composition of congruent vaporization for T_2 . From measured total pressures and the integrated changes in partial pressure with time, it is possible to calculate the small compositional changes. Fig. 5 shows the conclusions from this study: at approximately 1230°K the composition for congruent vaporization shifts by about 0.4 atomic percent sulfur across a miscibility gap that had previously been unknown. At lower temperatures the composition for congruent vaporization shifts by about 0.01 atomic percent sulfur per 100°K; at higher temperatures the composition shifts by the same amount for a 5°K change.

It is obvious that the properties of a semiconductor will change if it is heated at high temperatures in contact with a substance with which it reacts to form one or more new phases. Because of the sensitivity of semiconductor properties to composition, significant property changes may also occur when a semiconductor is heated in contact with a phase with which

it undergoes no gross chemical reactions. This point can be illustrated by reference to Fig. 6, the β Ti-B-C ternary phase diagram at about 1500°C. Because solution regions for this system are wide, the effects we wish to describe can be easily seen. Systems with narrow solution regions would show similar behavior. Compositions connected by the straight (tie) lines of Fig. 6 will not react with each other, but any of the solids not so connected can undergo reaction. Thus, for example, because carbon and TiB are not shown connected by a tie line while the TiB_2 and TiC phases are connected, one knows from the phase diagram that when carbon and TiB are heated together they will react to form TiB_2 and TiC. The TiB_2 and TiC phases are stable toward reaction with each other only when the particular composition of each phase corresponds to the opposite ends of the same tie line. Thus, for example, the TiC phase if prepared with a carbon content near the low end of its solution range would react with TiB_2 to form some TiB and a TiB phase of increased carbon content, and a TiC phase prepared with higher carbon content will lose titanium to, or gain titanium from, the TiB_2 phase until the compositions of the two phases are joined by the same tie line. Because semiconductor properties are sensitive to small compositional changes the kind of action just described might cause significant changes in electrical properties while causing compositional changes that go unnoticed.

When a semiconductor must be used at high temperatures in contact with another phase, it is important to remember that solids which are essentially insoluble in each other at low temperatures may have significant solution ranges at high temperatures. Most of us are accustomed to think that a phase such as calcite ($CaCO_3$) in the absence of impurities has an essentially constant composition. But recently Shukla and Searcy⁵ were able to measure

the variation in the CaO-CO₂ ratios in solid calcite as a function of temperature and CO₂ pressure. They showed that the solubility of CaO in CaCO₃ increased from about 3×10^{-5} mole percent at 830°K to about 9×10^{-4} mole percent at 1000°K. As expected from thermodynamic theory, the logarithm of the CaO solubility is a linear function of 1/T. If the same temperature dependence is assumed to persist to the eutectic temperature, about 1240°C⁵, the solubility is predicted to extend to as much as 0.7 mole dissolved CaO per mole of calcite.

The kind of exponential increase in low solubilities with temperature just illustrated can be expected in any solid state system containing two or more phases, including of course systems that incorporate composition-sensitive semiconductors, if these systems are used at very high temperatures.

Additional problems can arise if a semiconductor is subject to exposure to another phase (solid, liquid or gas) in a temperature gradient or in a thermal cycling operation. Because the two phases dissolve more of each other at the high temperature and less at the lower, solution and reprecipitation reactions may significantly change the form of the grains at the interface boundary. These interfacial changes can cause serious degradation of mechanical properties as well as of electrical properties.

A rather dramatic example of compositional change in a temperature gradient has been observed for α Zr and the zirconium hydride phase which is used as a moderator for nuclear reactors⁶. α -Zr dissolves about 2% to 8% H at 400° to 500°C and the minimum H/Zr atomic ratio in the α phase is about 1.4 in that temperature range. For the sample of Fig. 7 the original H:Zr ratio was 1.2, which corresponds to a two-phase mixture of the α and

γ phases. After a period of from 264 to 1220 hours in a temperature gradient extending from 400° to 500°C, the H:Zr ratio at the hot end of the sample was only about 0.4, whereas at the cool end it had risen to about 1.5, and the α phase had disappeared as a result. For Zr-H specimens the dimensional changes are large enough to cause deformation⁷. The dimensional changes in a compound semiconductor in contact with a second phase may not have the same potential for catastrophic mechanical failure but they are certainly undesirable, and the change in band structure may render the device inoperative in its circuit.

ACKNOWLEDGMENT

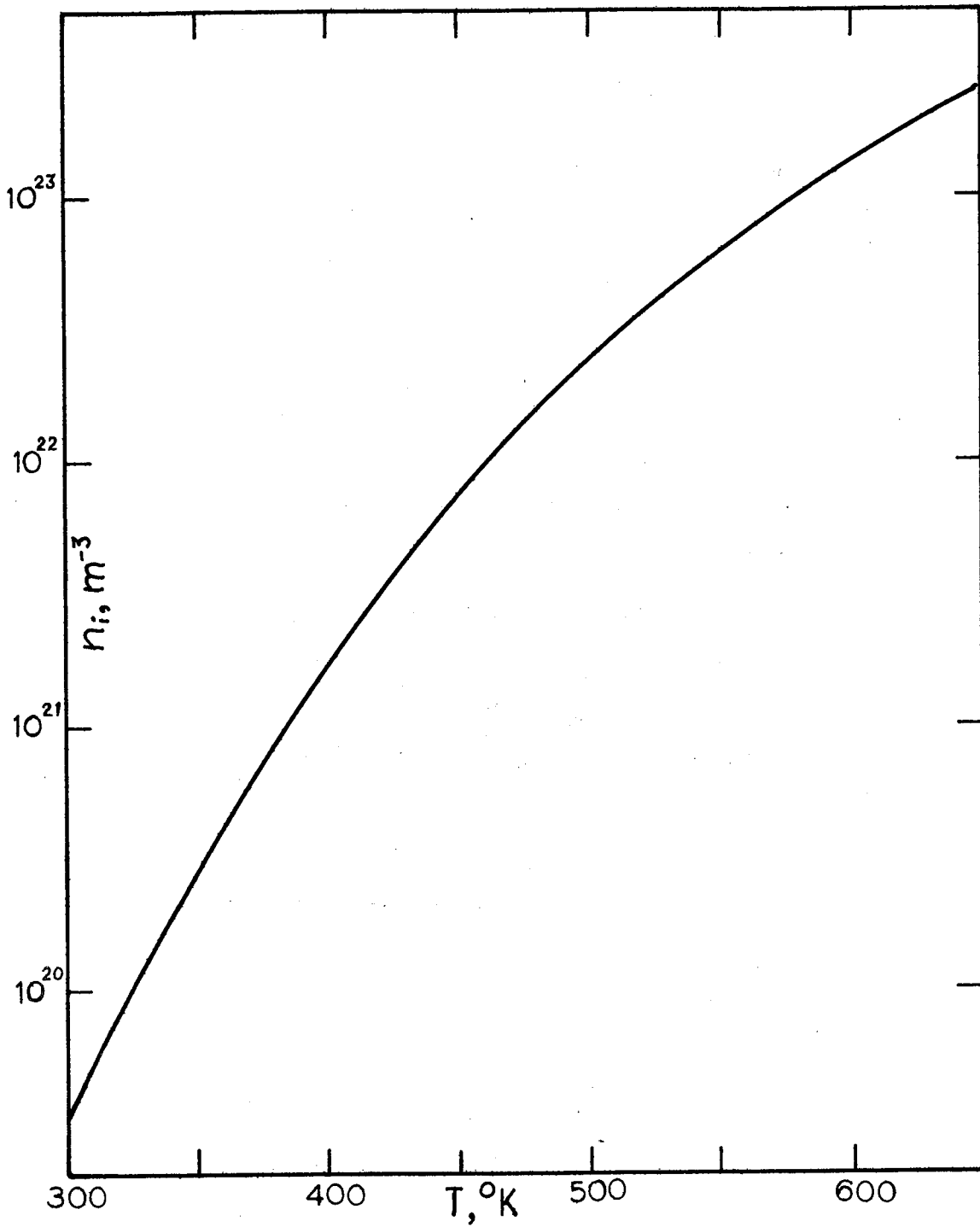
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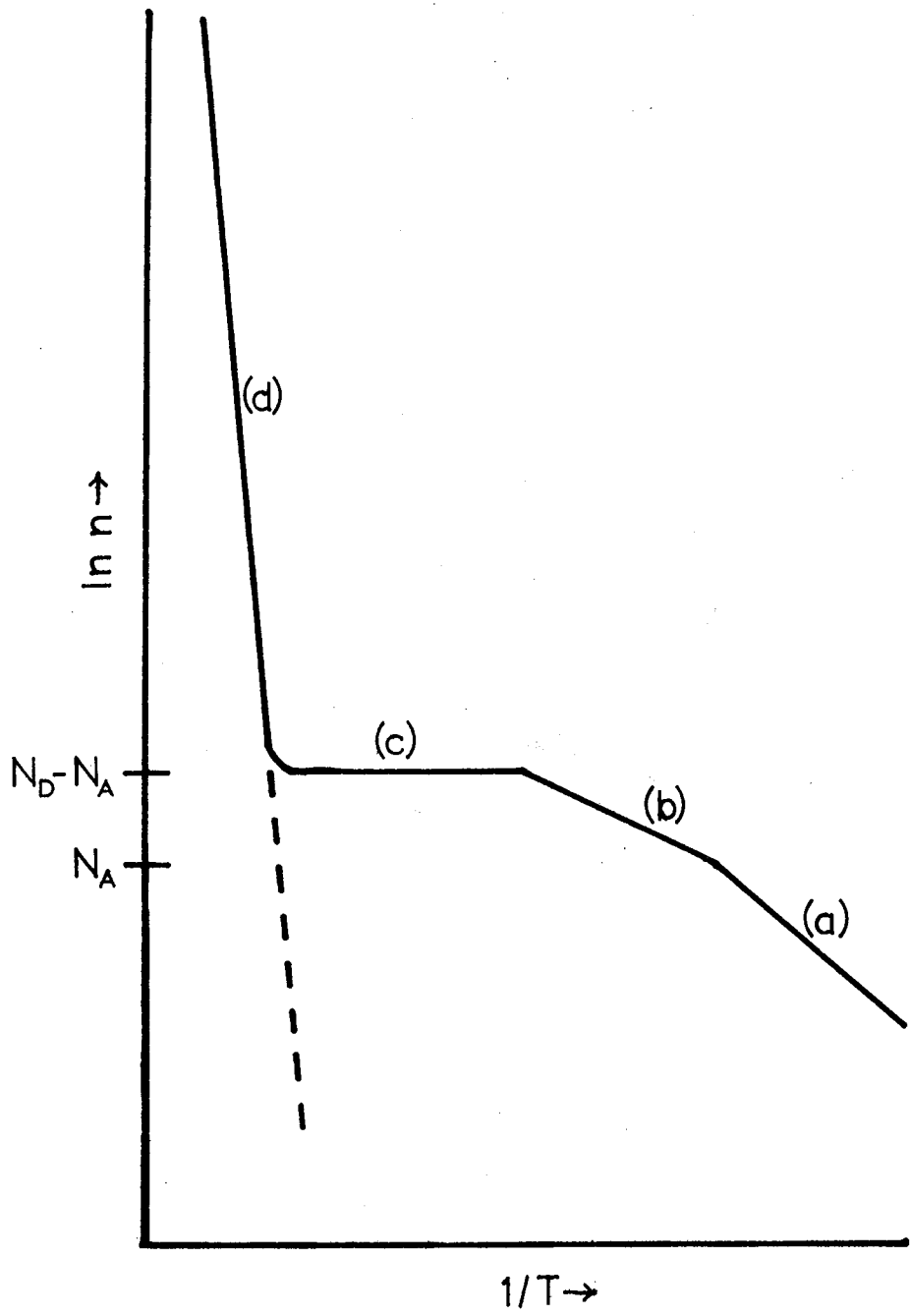
Figure Captions

- Fig. 1. Plot of intrinsic carrier concentration, n_i , as a function of temperature for germanium.
- Fig. 2. Variation of carrier concentration as a function of inverse temperature for a doped semiconductor.
- Fig. 3. Carrier concentration in PbS as a function of S_2 pressure at 1000° and 1200°K.
- Fig. 4. Ion Intensity (Ga_2S^+ and S_2^+) versus time with the temperature plotted below.
- Fig. 5. Congruent vaporization composition of Ga_2S_3 as a function of temperature.
- Fig. 6. The $\beta Ti-B-C$ ternary phase diagram at 1500°C.
- Fig. 7. Compositions of $TiH_{1.2}$ samples kept in a temperature gradient for 226, 336 and 1220 hours.



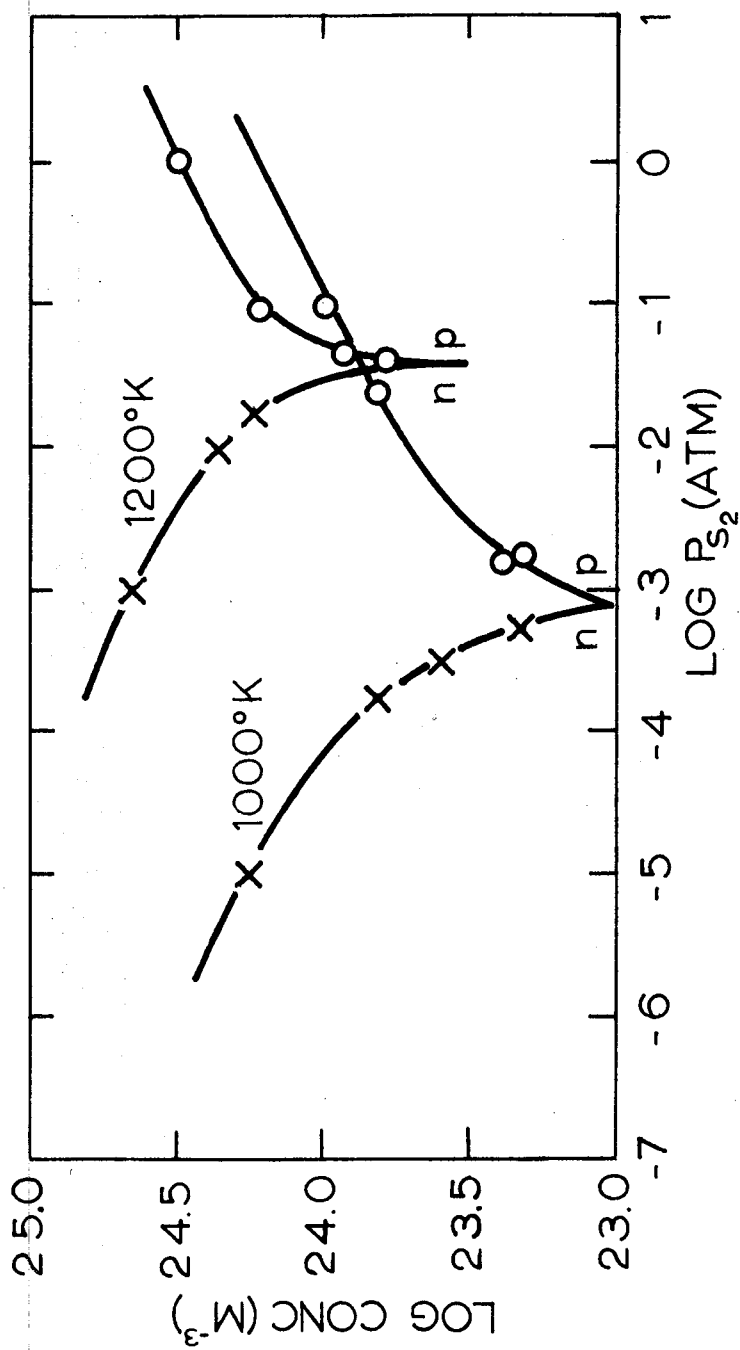
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Fig. 1



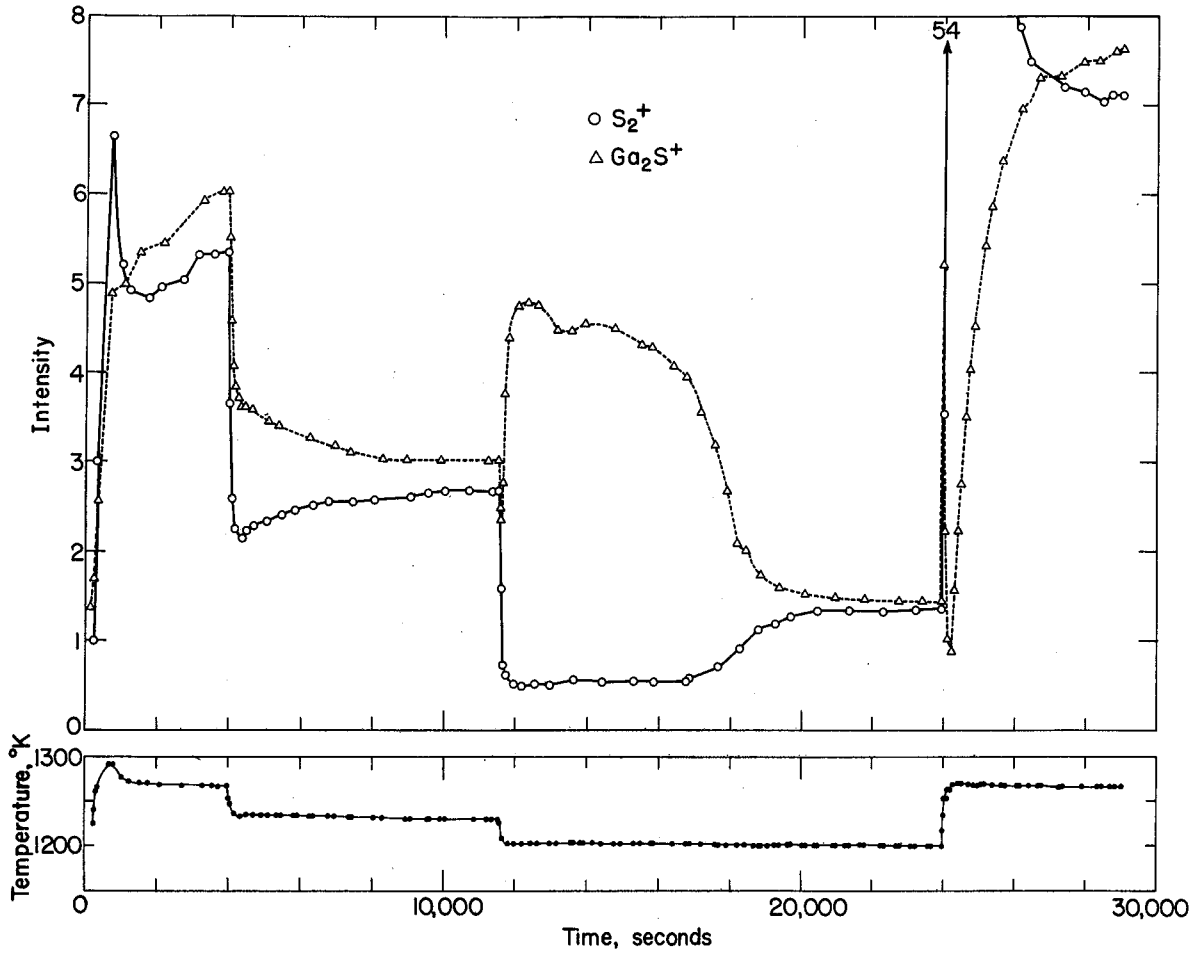
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Fig. 2



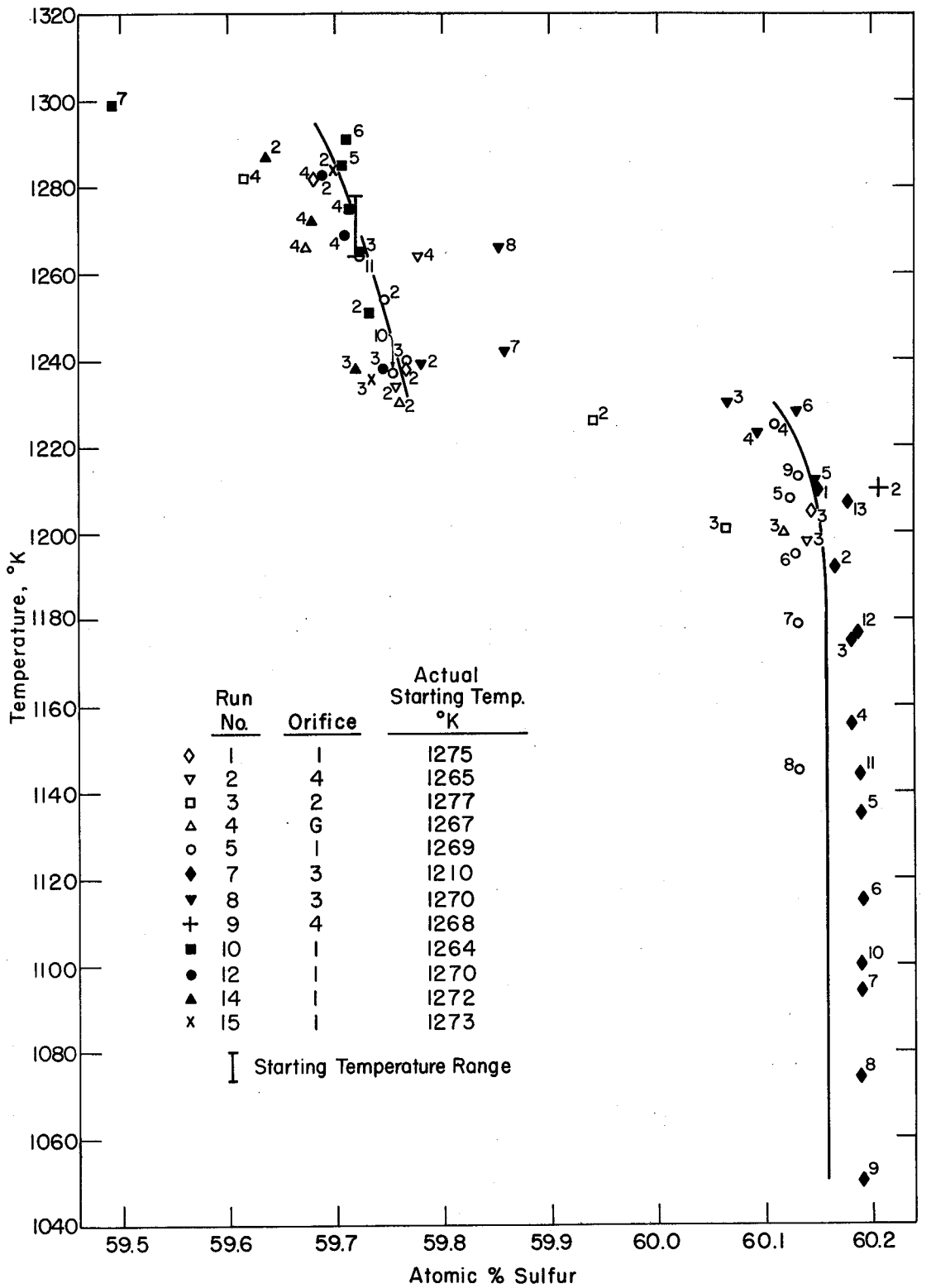
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Fig. 3



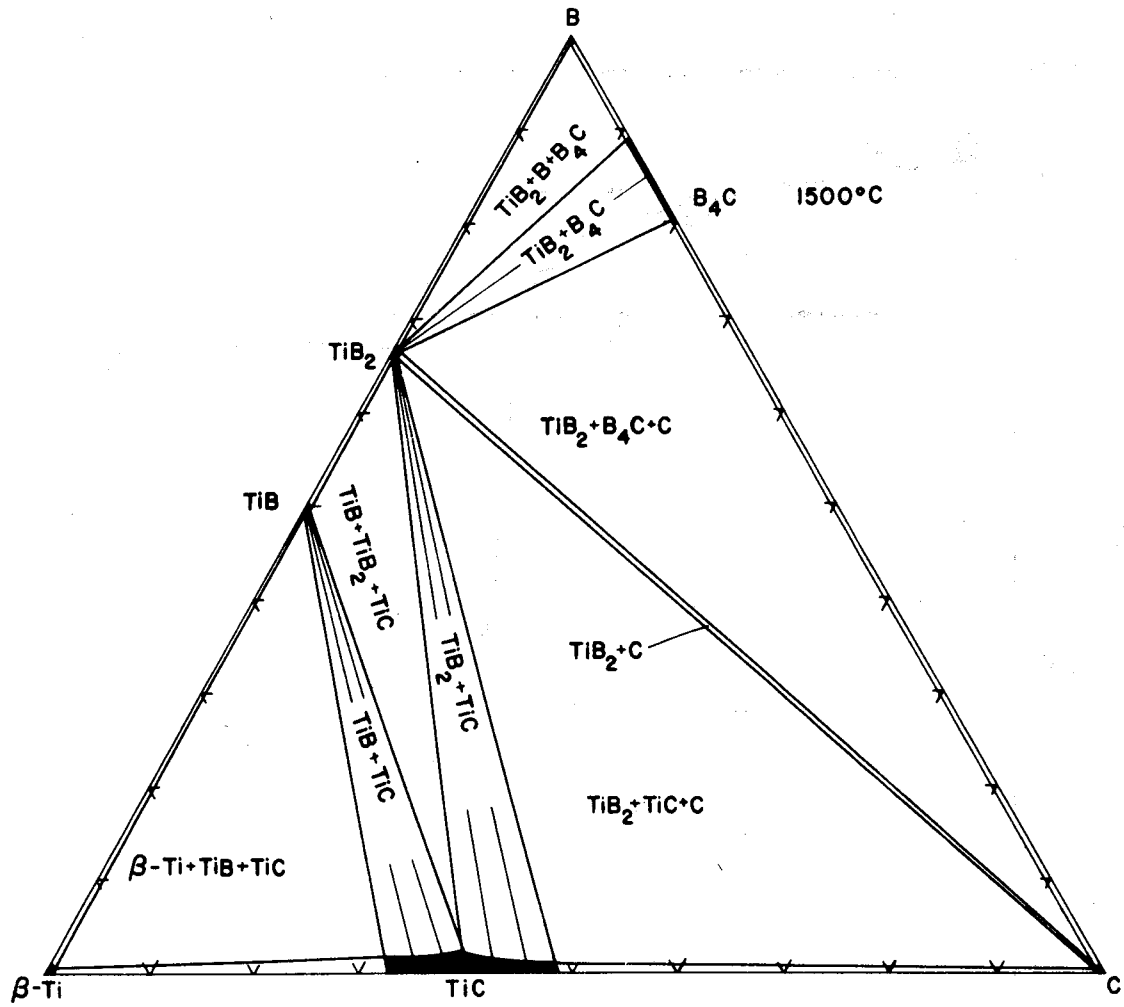
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Fig. 4



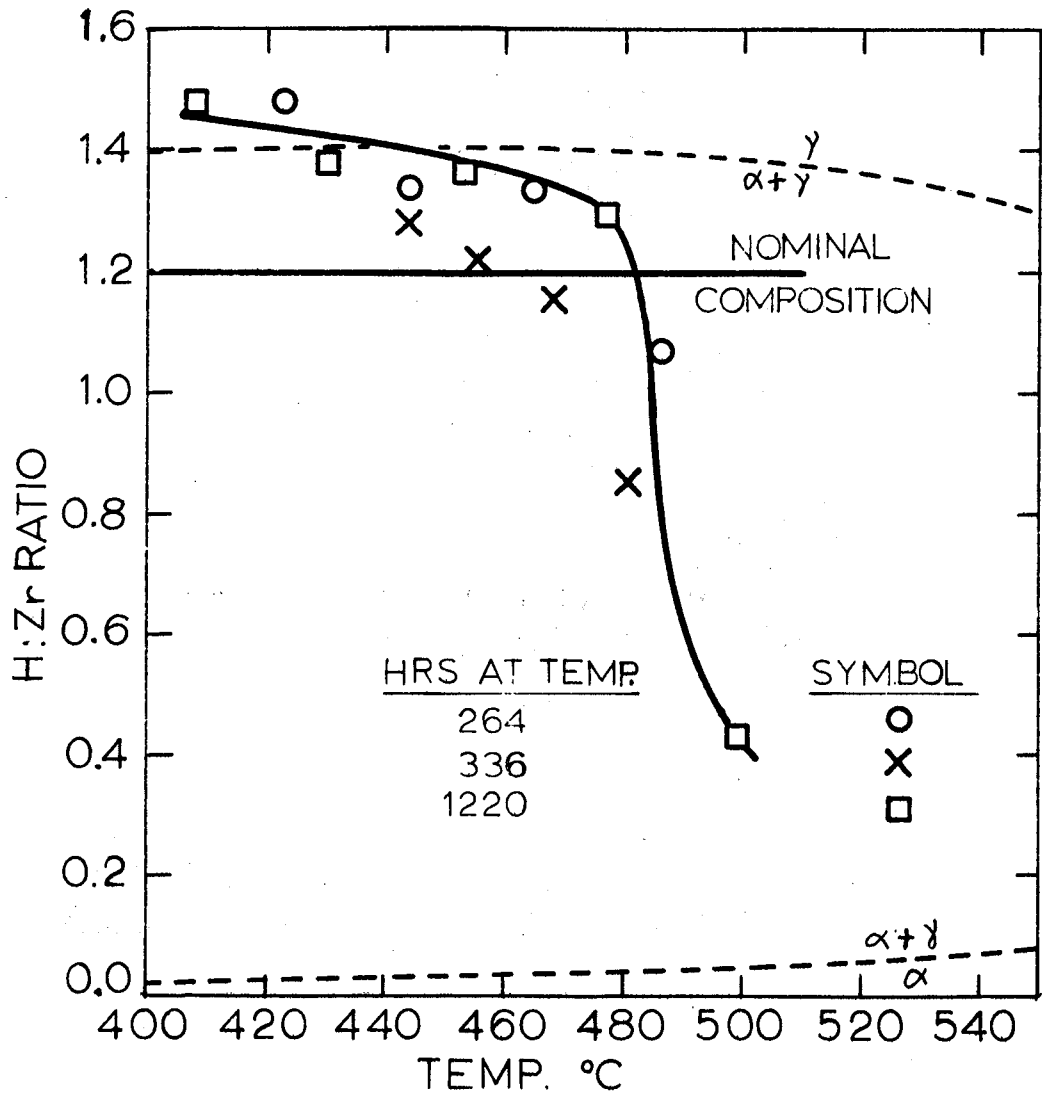
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Fig. 5



XBL 809-11674

Fig. 6



XBL 8010-12371

Fig. 7