

Changes in Electrical Conductivity of a Synthetic Basalt during Melting¹

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The electrical conductivity of a synthetic basalt has been determined at atmospheric pressure in air at temperatures between 700° and 1600°C. The conductivity increases by about 2 orders of magnitude in the melting interval between 1130° and 1263°C. It is suggested that partial fusion in the seismic low-velocity zone of the upper mantle may account for the correlation of increased electrical conductivity with development of this zone.

Recent geomagnetic deep-sounding studies with large arrays of magnetometers have shown the presence of several magnetic variation anomalies in the western United States that are related to lateral changes in the electrical conductivity of the earth's upper mantle [Reitzel *et al.*, 1970; Porath *et al.*, 1970; Porath and Gough, 1971]. There are several factors that may contribute to variations in the electrical conductivity of the upper mantle, such as temperature, compositional changes, phase changes, pressure, and partial fusion. The effect of partial fusion on the electrical conductivity of probable mantle constituents is of particular interest. There is a general correlation between enhanced electrical conductivity, high heat flow, and development of the seismic low-velocity zone in the upper mantle [Porath and Gough, 1971], and partial fusion in the low-velocity zone has been suggested to account for the relative magnitudes of *P* and *S* travel-time delays in tectonic regions of the western United States [Hales and Doyle, 1967].

In order to test the effect of melting on conductivity in the upper mantle, it would be most desirable to study a peridotite composition through its melting interval at high pressure. Because of experimental difficulties in measuring the conductivity of liquid samples at high

pressures, we have chosen instead to carry out a preliminary study on the conductivity of a basalt composition through its melting interval at 1 atm pressure. Basalt melts at a low enough temperature that measurements considerably above the liquidus are possible. Although the data cannot be applied directly to conductivities in the upper mantle, the results may indicate the type of effects to be expected during melting of mafic silicate compositions.

PREVIOUS WORK

The first experiments on the behavior of electrical conductivity of silicates during melting were published by Barus and Iddings [1892]. Their measurements are stated to have been made while decreasing the temperature at a rate sufficient to prevent crystallization below the liquidus. Their rhyolite and andesite compositions showed no discontinuity in the conductance in passing from the liquid to glassy states. However, their data for basalt suggest the existence of a discontinuity at a temperature of 1124°C.

Volarovich and Tolstoi [1936] measured the electrical conductivity of a basaltic lava from Mt. Vesuvius at temperatures from 1400° to 945°C. Experimental details are not given, but they found a small discontinuity at about 1000°C which they attributed to crystallization (Figure 3, curve 4).

Nagata [1937] measured the conductivity of two lavas from about 1250°C to below 600°C. During heating at a rate of about 300°C/hour, he observed a small discontinuity in the conduc-

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tivity at about 1130°C, but no discontinuity was found during cooling at the same rate. His curve for one of these lavas, a basaltic lava from Mihara, is shown in Figure 3 (curves 2 and 3).

Murase [1962] measured the conductivity of several lavas of varying composition at temperatures from 800° to 1400°C and found an approximately linear relation between log conductivity and reciprocal temperature with no discontinuity in the melting interval. He did not give the physical state of the various lavas below their solidus temperatures, but the heating and cooling rates were 300°C/hour, and so the more viscous rhyolite compositions probably were in a completely glassy state. The less viscous basalt and andesite melts may have crystallized partially on cooling. His curves for two basaltic rocks are shown in Figure 3 (curves 1 and 5).

The above studies suggest that melting has either no effect or at most only a small effect on the electrical conductivity. However, measurements of albite, granite, and basalt at a variety of pressures by *Lebedev and Khitarov* [1964], *Khitarov and Slutskiy* [1965], and *Khitarov et al.* [1970] reveal sharp increases in electrical conductivity during melting. *Khitarov and Slutskiy* [1965] found a difference in conductivity of about 1 order of magnitude between crystalline and partially glassy basalt at the same temperature, and a difference of up to 4 orders of magnitude between crystalline and glassy albite. These results suggest that the failure of previous investigators to observe a sharp increase in conductivity during melting was due to the glassy state of their samples below solidus temperatures. *Lebedev and Khitarov* [1964] compared the conductivity of crystalline and liquid granite at 1 atm and observed an increase of more than 3 orders of magnitude during melting. The data of *Khitarov et al.* [1970] on three basalts do not extend above liquidus temperatures, but their measurements at 28 kb suggest that melting may cause an abrupt increase of 1 to 2 orders of magnitude in the conductivity.

PREPARATION OF BASALT COMPOSITION

We have measured the variation of electrical conductivity with temperature for a synthetic basalt whose composition is given in Table 1.

TABLE 1. Synthetic Basalt Composition

Composition as Weighed		Spectrochemical Analysis*	
Oxide	Amount, wt. %	Element	Amount, ppm
SiO ₂	48.06	B	20 to 40
Al ₂ O ₃	17.21	Cu	5
Total Fe as Fe ₂ O ₃	10.69	Sr	60
MgO	8.62	Ba	<5
CaO	11.37	Cr	<10
Na ₂ O	2.37	Ni	<5
K ₂ O	0.25	V	<10
TiO ₂	1.17	Zr	<10
P ₂ O ₅	0.10	Yb	<1
MnO	0.16	Y	<10
Total	100.00	Ag	<1
		Pb	<20
		Sn	<20
		Zn	<100

*N. H. Suhr, analyst.

The basalt was made up to be identical to the composition (reduced to 100%, water free) of the chilled margin of the Skaergaard intrusion [*Wager and Brown*, 1967, p. 152]. It has a composition very close to much of the basalt on the ocean floors [*Engel et al.*, 1965] and to various other basalts from Japan, California, and the Galapagos Islands [*Presnall*, 1966, Table 3]. The Fe₂O₃/FeO ratio is unknown, but it is considerably higher than for natural basalts, because the sample was exposed to air during the high-temperature conductivity measurements.

The basalt was prepared from Fisher certified reagent chemicals except as indicated below. KHCO₃ was melted together with SiO₂ (Corning code 7940 fused silica) to make K₂Si₂O₆ according to the method of *Schairer and Bowen* [1955], and this was used as a source of both K₂O and SiO₂. Na₂Si₂O₆ was prepared in the same way from NaHCO₃ and SiO₂ [*Schairer and Bowen*, 1956]. Corning fused silica was used to make up the remaining SiO₂ required. Mn₂O₃, obtained by firing Mn₂O₄ at 1100°C, was used as a source of manganese. Ca₂P₂O₇, prepared according to the method of *St. Pierre* [1953], was used as a source of phosphorus and calcium, and the remaining calcium needed was weighed in as CaCO₃. A spectrochemically analyzed (less than 0.02% impurities) lot of Buehler γ -alumina polishing compound was used as a source of Al₂O₃. MgO was prepared by dissolving pure Mg metal in HNO₃, evaporating the solution to dryness, and firing the resulting magnesium

nitrate over a Fisher burner to drive off all NO_x . The required amounts of iron and titanium were weighed as Fe_2O_3 and TiO_2 .

A homogeneous basaltic glass was prepared by firing the above materials in a platinum crucible at 1330°C in air for 6 hours. No measurable amount of iron is lost from the silicate liquid to the platinum crucible under these conditions [Taylor and Muan, 1962].

LIQUIDUS AND SOLIDUS TEMPERATURES

The liquidus and solidus temperatures of the basalt were determined by quenching experiments in air and in CO_2 (Table 2). In these experiments, each sample was suspended as a drop of liquid held by surface tension within a loop of fine (0.002-inch-diameter) platinum wire. The mass of wire in contact with the melt (about 0.0005 gram) was small enough relative to the sample (about 0.03 gram) that iron loss from the sample to the platinum wire was negligible. Each sample was prepared by wrapping a fine platinum wire once around a sintered cylindrical pellet and melting the pellet into a completely liquid drop at about 1350° . The sample was then removed rapidly from the furnace for later use in an equilibrium experiment. Thus the starting material for each equilibrium run was a glass sphere.

Table 2 shows that the liquidus temperature in CO_2 (approximately 1246°) is only about 17° lower than that in air (approximately 1263°), even though the primary phase changes from spinel to plagioclase and the oxygen fugacity is about 3 orders of magnitude lower. The solidus temperatures are more uncertain because of

difficulty in detecting trace amounts of glass in the quenched products. Also, at temperatures below the solidus, reaction rates are slow and there may not have been complete equilibration of the furnace atmosphere with the interior of the glass sphere. It was finally decided to base the determination of solidus temperature on microscopic examination of the surface topography of the recrystallized glass spheres. Below the solidus, the surface was smooth but obviously recrystallized. Above the solidus, the surface was irregular owing to movement of small amounts of interstitial liquid between crystals. By this criterion, the solidus temperature in air (about 1130°) was found to be not measurably different from that in CO_2 (about 1125°). Although these temperatures are less certain than the liquidus temperatures, they illustrate that the solidus temperature, like the liquidus temperature, is not sensitive to changes in the $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio. The reason for demonstrating this fact will become apparent when the conductivity measurements are discussed.

CONDUCTIVITY MEASUREMENTS

The basalt glass was melted into a platinum crucible with a hemispherical bottom that served as one electrode for the conductivity measurements. The other electrode was a smaller hemispherical crucible immersed into the liquid in the center of the larger crucible. This gave a symmetrical electrode arrangement (Figure 1) from which resistivities could easily be calculated from resistances. The sample was completely melted at 1350°C , rapidly cooled in air

TABLE 2. Quenching Experiments on Synthetic Basalt Composition of Table 1

Temperature, $^\circ\text{C}$	Time, hours	Furnace Atmosphere	Log Oxygen Fugacity, atm	Phases Present*
1270	22	Air	-0.68	gl
1256	21	Air	-0.68	sp + gl
1144	49	Air	-0.68	sp + hem + plag + px + ol(?) + gl(?)
1124	72	Air	-0.68	sp + hem + plag + px + ol(?)
1251	22	CO_2	-3.64†	gl
1240	26	CO_2	-3.68†	plag + gl
1140	48	CO_2	-4.14†	sp + hem + plag + px + ol(?) + gl(?)
1120	72	CO_2	-4.91†	sp + hem + plag + px + ol(?)

*gl, glass; sp, spinel; hem, hematite; plag, plagioclase; px, one or more pyroxenes; ol, olivine.

†Calculated from data of Robie and Waldman [1968].

to form a glass, and finally held at 1050°C in air for two weeks to produce a completely crystalline material consisting of plagioclase, pyroxene, hematite, spinel, and olivine(?). Because crystalline basalt has a volume about 4–7% less than a glass of the same composition [Daly *et al.*, 1966, p. 21], there would seem to be the possibility of forming large cavities and cracks during the crystallization at 1050°C. To check this, the level of the sample's surface was measured before and after crystallization. It decreased without visible fractures by an amount equivalent to a volume decrease of approximately 7%, indicating that the glass flowed sufficiently in its supercooled state to prevent fracturing and cavity formation during crystallization.

After crystallization for two weeks at 1050°C and without removing the sample from the furnace for inspection, conductivity measurements were taken in air with decreasing temperature down to 705°C (Figure 2). Measurements were then continued with increasing temperature from 1050° to 1585°C. Finally, measurements were taken while cooling the sample back to 1050°C from 1585°C. Heating and cooling rates were approximately 150°C/hour.

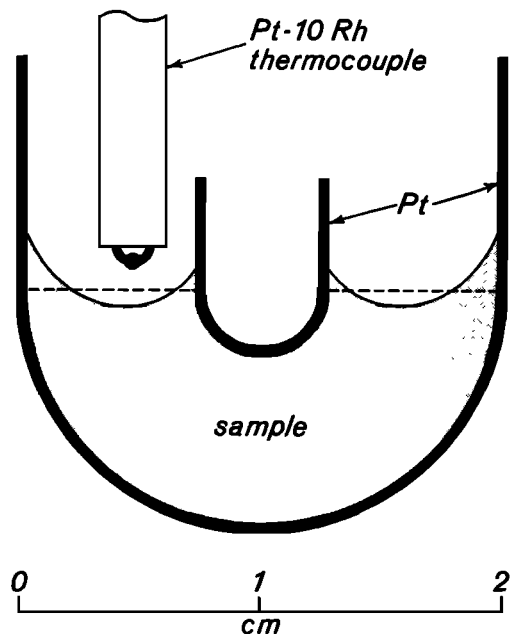


Fig. 1. Cross section of sample showing hemispherical electrode arrangement.

Two other sets of measurements were carried out to examine the effect of different cooling rates through the crystallization interval. In one case, conductivity was measured while decreasing the temperature from 1300°C down to 666°C at a rate of about 300°C/hour. In the other, the sample was taken above its liquidus temperature to produce complete melting, and then the temperature was decreased from 1207°C to 1160°C in a stepwise fashion, time being allowed at each temperature for crystallization to occur (indicated by a close approach to stabilization of the resistance). Times required to achieve a reasonably stable resistance at each temperature varied from 30 min to 5 hours, total cooling time from 1228° to 1160°C being about 8 hours. However, even these times were not sufficient to achieve complete chemical equilibrium at each temperature.

A General Radio 1650-A impedance bridge with a stated accuracy of $\pm 1\%$ was used to make the resistance measurements. Direct current measurements drifted owing to polarization when the sample was either glassy or liquid but not when it was completely crystalline. To eliminate polarization, 1000-Hz ac resistance measurements were taken, and these are the only data reported here.

DISCUSSION

The heating and cooling rates were such that complete chemical equilibrium was not attained at any temperature. Experiments above the liquidus temperature on this basalt indicate that about 10 hours would be necessary for complete equilibration of the $\text{Fe}_3\text{O}_4/\text{FeO}$ ratio at each temperature. The equilibrium $\text{Fe}_3\text{O}_4/\text{FeO}$ ratio varies with temperature, and even though complete equilibrium was not achieved, some variation in the $\text{Fe}_3\text{O}_4/\text{FeO}$ ratio would be expected during the heating and cooling cycles. Thus, if the $\text{Fe}_3\text{O}_4/\text{FeO}$ ratio strongly affects conductivity, the data on heating should not reproduce those on cooling. Our data on heating and cooling in the liquid region are nearly identical, and so either the heating and cooling rates were sufficiently rapid that the $\text{Fe}_3\text{O}_4/\text{FeO}$ ratio changed only a small amount or the conductivity is not strongly dependent on the $\text{Fe}_3\text{O}_4/\text{FeO}$ ratio.

Figure 2 shows that the conductivity increases abruptly about 2 orders of magnitude in the

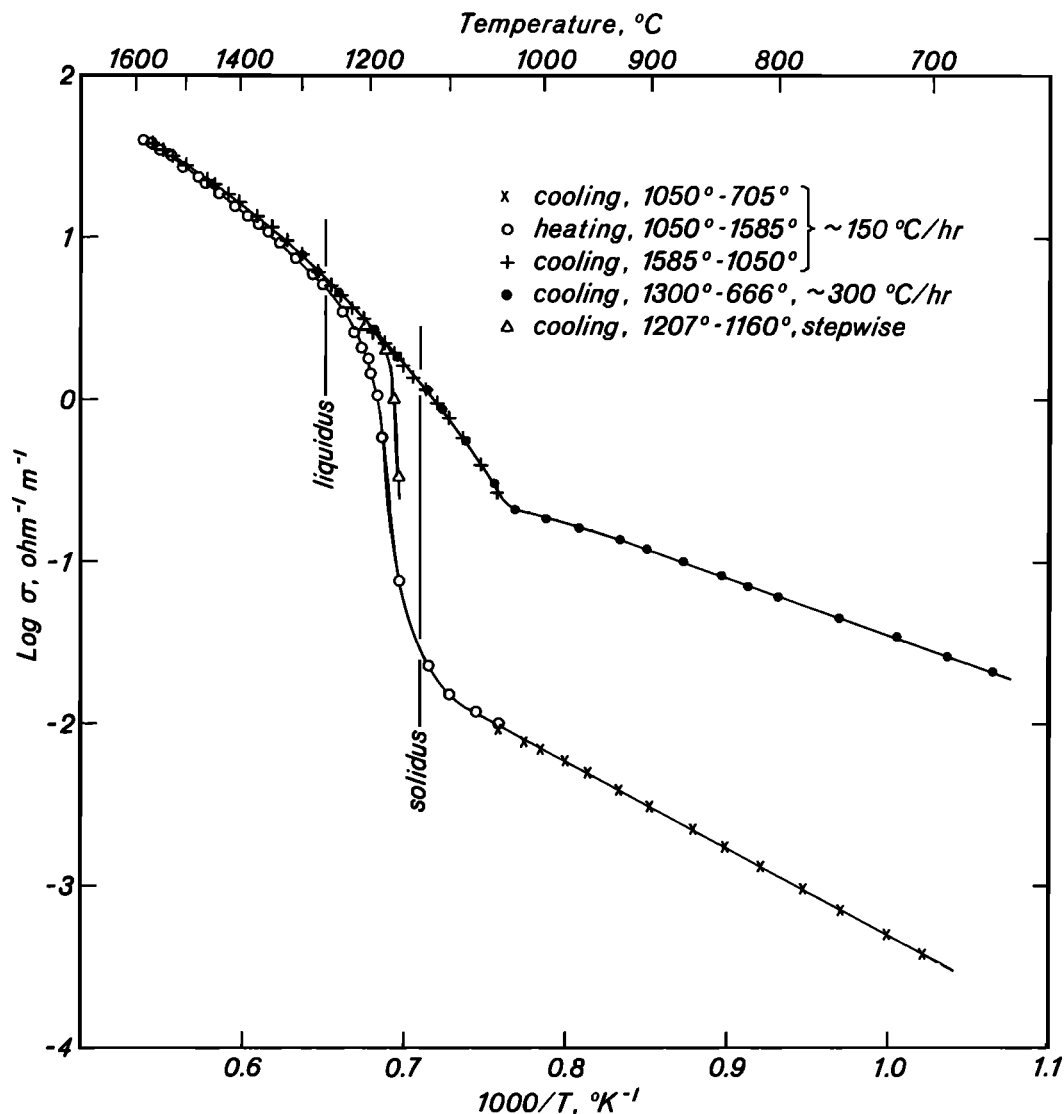


Fig. 2. Variation of conductivity with temperature for a synthetic basalt. Below the solidus, the upper curve is for predominantly glassy material and the lower curve is for completely crystalline material.

melting interval. As was shown earlier, the solidus and liquidus temperatures are not strongly dependent on the $\text{Fe}_3\text{O}_4/\text{FeO}$ ratio, and so the correlation of conductivity increase with melting is valid even though our heating and cooling rates were not slow enough to achieve complete equilibration of the $\text{Fe}_3\text{O}_4/\text{FeO}$ ratio at each temperature.

The data collected while cooling at 300°C/hour from 1300°C to 666°C (Figure 2) are for

a predominantly glassy material below the solidus, and the conductivities are between 1 and 2 orders of magnitude greater than for completely crystalline material at corresponding temperatures. The data collected from 1585°C to 1050°C at a cooling rate of 150°C/hour fall on the same curve as those collected at 300°C/hour, indicating that crystallization does not significantly increase at the slower cooling rate. However, when time is allowed

for crystallization, as indicated by a close approach to stabilization of the resistance at each temperature, conductivities fall close to the curve for heating of crystalline material.

In the completely crystalline state, the conductivity can be described by

$$\sigma_{xl} = \sigma_1 e^{-E_1/kT}$$

with $\sigma_1 = 110 \text{ ohm}^{-1} \text{ m}^{-1}$ and $E_1 = 1.06 \text{ ev}$ (k is Boltzmann's constant, T is absolute temperature). In the completely liquid region, the variation of $\log \sigma$ with $1/T$ is not quite linear, but the conductivity can be described approximately by

$$\sigma_{liq} = \sigma_2 e^{-E_2/kT}$$

with $\sigma_2 = 3.8 \times 10^6 \text{ ohm}^{-1} \text{ m}^{-1}$ and $E_2 = 1.46 \text{ ev}$.

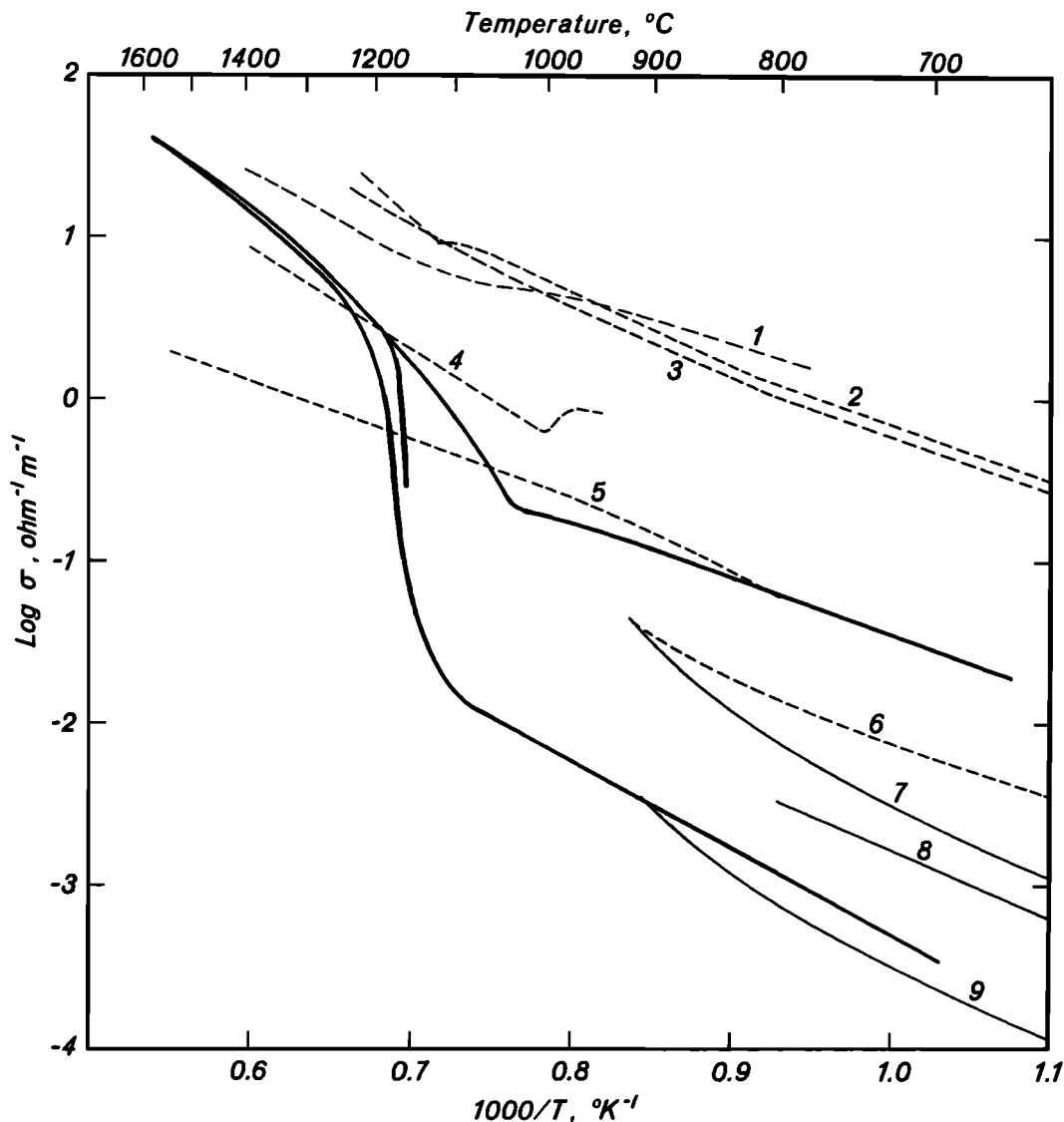


Fig. 3. Comparison of present data (heavy curves) with previous data on liquid and glassy basalt (dashed curves) and crystalline basalt (solid curves) at 1 atm pressure. In the absence of information in the original reference, curve 8 is assumed to be for crystalline material. Curves 1 and 5 are from Murase [1962]; curves 2 and 3 are heating and cooling curves, respectively, for the same sample [Nagata, 1937]; curve 4 is from Volarovich and Tolstoi [1936]; curves 6, 7, and 9 are from Coster [1948]; and curve 8 is extrapolated to 1 atm from high-pressure data of Parkhomenko [1967, p. 171].

The lower-temperature part of the curve for predominantly glassy material is linear and can be described by

$$\sigma_{gl} = \sigma_0 e^{-E_a/kT}$$

with $\sigma_0 = 115 \text{ ohm}^{-1} \text{ m}^{-1}$ and $E_a = 0.72 \text{ ev}$.

Figure 3 shows a comparison of our data with those of previous investigators on basaltic compositions at 1 atm pressure. Agreement with previous data appears satisfactory, but the wide spread of curves makes detailed comparisons difficult. This wide spread could be caused by differences in composition, grain size, preferred orientation of crystals, and cracks. Despite the large differences in the previous data, glassy and liquid basalts appear as a group to have conductivities about 2 orders of magnitude greater than crystalline basalt and gabbro, in support of our data.

The abrupt change in slope of our upper curve at 1050°C bears some resemblance to the changes in slope of curves 1, 2, and 4. This change in slope occurs well below the solidus temperature and is apparently due to some change in conductivity mechanism in the glass unrelated to crystallization effects.

The sharp increase of conductivity we observe during melting of basalt is the same type of result obtained for albite, granite, and basalt at high pressures by Lebedev and Khitarov [1964], Khitarov and Slutskiy [1965], and Khitarov et al. [1970], suggesting that such changes may be typical of a wide variety of silicate compositions at both low and high pressures. Sharp increases in conductivity during melting have also been found for a number of other semiconducting materials [Gubanov, 1965, pp. 6-12].

It has been argued by several investigators that the seismic low-velocity zone in the mantle is a region of partial melting [Hales and Doyle, 1967; Anderson and Sammis, 1970; Nur, 1971], and Porath and Gough [1970] have shown that there is a general correlation of high electrical conductivity in the mantle with development of this zone. Our data indicate that this enhanced electrical conductivity could be explained by partial melting in the low-velocity zone.

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