The Electrical Conductivity of the System CaO-CaF_2

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In studies of the system $CaO-CaF_2$[1], the electrical conductivities of the different mixtures were measured. The results are shown in Fig. 1 for the temperatures 1 500, 1 515, 1 530 and 1 545 ° C, all well over the melting points. The interesting thing is that in spite of its well-known low conductivity [2] ($\varkappa$ = 0.175 ohm^{-1} cm^{-1} at the melting point 2 570 ° C) CaO in these mixtures increases the conductivity. We also see that at a certain point on an isotherm, the conductivity rapidly increases and at a still higher percentage of CaO suddenly decreases.

The reasons for these very interesting features can be explained if we remember that the ionic radii of F^- and O^{2-} are nearly equal (r_{F^-} = 1,36 Å and $r_{O^{2-}}$ = 1.40 Å [3]). At lower percentages of CaO we can suppose that the oxygen ions can be built in into the "liquid lattice" of the fluorine ions, similarly to what happens in the solid state in mixed crystals of KCl-$SrCl_2$[4], where the cation vacancies produced by the unequal charges of the cations increase the ionic conduction. In our case the unequal charges of O^{2-} and F^- will also cause anion vacancies and an increase in the conduction. A consequence of these vacancies must be a lowering of the density of the melt. This lowering is a linear function of the composition. If we know the density of molten CaF_2, we can compute what densities the melts should be without vacancies and with vacancies. In Table 1 this has been done for 1 545 ° C

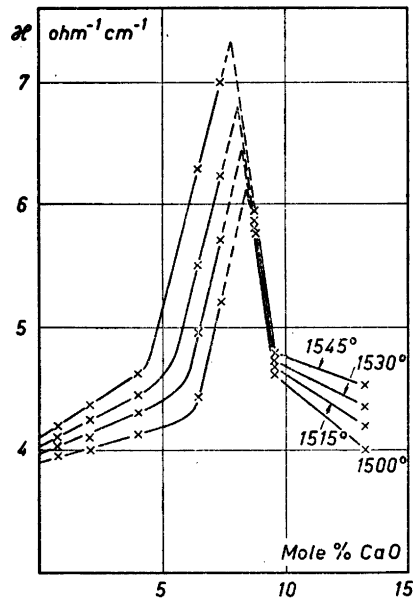

Fig. 1. Electrical conductivities at different temperatures.

Table 1.

Mole fraction CaO	Densities observed	Densities computed without vacancies	Densities computed with vacancies
0.0000	2.75	2.75	2.75
0.0205	2.68	2.73	2.68
0.0400	2.59	2.72	2.62
0.0650	2.53	2.70	2.53
0.0735	2.50	2.69	2.51
0.0956	2.63	2.68	2.44

and compared with observed values. We see that the agreement is excellent up to x_{CaO} = 0.0735. But at x_{CaO} = 0.0956 the observed density disagrees and is much higher than the computed. If we return to Fig. 1 it is seen than there is an increase in the conductivity with CaO concentration — caused by the movement of fluorine ions through the vacancies — at the beginning, there is a slight linear rise which is however followed by a more rapid increase at higher concentrations. The concentration of these vacancies has a limit, after which this type of "liquid lattice" breaks down and the conductivity decreases and the density increases. This maximum number of vacancies decreases with increasing temperature, *i. e.* with greater thermal agitation.

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