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Abstract

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PHYSICAL CHEMISTRY

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REGULARITIES IN THE VARIATION OF CERTAIN PHYSICOCHEMICAL PROPERTIES DURING THE MELTING OF SEMICONDUCTORS OF DIFFERENT STRUCTURAL GROUPS*

(Presented by Academician I. I. Chernyaev, 15 IX 1964)

This communication discusses changes in certain physicochemical properties during the melting of semiconductor compounds with structures of the ZnS, NaCl, and CaF_2 types. The groups of compounds were chosen so that it would be possible to trace the influence of the positions of the components in the periodic system and, consequently, the character of the chemical bond within each structural group.

The compounds AlSb, GaSb, InSb, GaAs, InAs, ZnTe, CdTe, CuJ, Ga_2Te_3 , and In_2Te_3 , which have a lattice of the ZnS type, were studied, as well as compounds

Table 1

Change in electrical conductivity and magnetic susceptibility during the melting of semiconductor compounds of different structural groups

T, melt- Compound and σ_{solid} , σ_{liq} , Structure, melting point, $\text{ohm}^{-1}\text{cm}^{-1}$, χ_{solid} , χ_{liq} , type, formula, °C, cm^{-1} , cm^{-1} , 10^6 , 10^6							T, melt- Compound and σ_{solid} , σ_{liq} , Structure, melting point, $\text{ohm}^{-1}\text{cm}^{-1}$, χ_{solid} , χ_{liq} , type, formula, °C, cm^{-1} , cm^{-1} , 10^6 , 10^6						
ZnS	AlSb	1080	$0.5 \cdot 10^2$	$1.2 \cdot 10^4$	1.31	1.16	NaCl	PbTe	917	$3 \cdot 10^2$	$1.5 \cdot 10^3$	0.17	0.13
ZnS	GaSb	705	$1 \cdot 10^2$	$1.6 \cdot 10^4$	1.27	1.00	NaCl	PbSe	1088	$2.5 \cdot 10^2$	$0.8 \cdot 10^3$	—	—
ZnS	InSb	525	10^3	$1.4 \cdot 10^4$	1.32	1.06	CaF_2	Mg_2Si	1102	$1.1 \cdot 10^3$	10^4	0.50	0.40
ZnS	GaAs	1280	10^3	10^4	1.24	0.85	CaF_2	Mg_2Ge	1115	$1.1 \cdot 10^3$	10^4	0.53	0.43

T, melt-								T, melt-							
Compound								Compound							
Structure	Formula	Point, °C	σ_{solid} , $\text{ohm}^{-1} \cdot \text{cm}^{-1}$	σ_{liq} , $\text{ohm}^{-1} \cdot \text{cm}^{-1}$	χ_{solid} , 10^6	χ_{liq} , 10^6		Structure	Formula	Point, °C	σ_{solid} , $\text{ohm}^{-1} \cdot \text{cm}^{-1}$	σ_{liq} , $\text{ohm}^{-1} \cdot \text{cm}^{-1}$	χ_{solid} , 10^6	χ_{liq} , 10^6	
ZnS	InAs	940	10^3	10^4	1.20	0.90		CaF ₂ Mg ₂ Si	780	$1.9 \cdot 10^3$	10^4	0.55	0.52		
ZnS	ZnTe	1240	5	10^2	1.37	1.25		CaF ₂ Mg ₂ P	550	$3.6 \cdot 10^3$	10^4	0.32	0.28		
ZnS	CdTe	1045	5	10^2	1.45	1.30									
ZnS	Ga ₂ Te	880	3	10^2	1.34	1.21									
ZnS	In ₂ Te	660	5	10^2	1.36	1.22									
ZnS	CuJ	605	3	3.5	—	—									

PbTe and PbSe, which have an NaCl lattice, and the compounds Mg₂Si, Mg₂Ge, Mg₂Sn, and Mg₂Pb, which have a lattice anti-isomorphous to CaF₂.

In selecting the objects, we set ourselves the task of studying the regularities in the changes of physicochemical properties during the melting of analogous compounds both with “cationic” and with “anionic” substitution, as well as the regularities in the variation of properties in isoelectronic series. The character of the change in electrical conductivity and magnetic susceptibility during the melting of the above-mentioned compounds is considered.

The studies showed (Table 1) that, during the melting of A^{III}Sb and A^{III}As compounds, the electrical conductivity increases sharply, reaching values on the order of $10,000 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$. On heating the melts of these compounds, the electrical conductivity decreases.

* The work was presented at the Third All-Union Conference on Semiconductor Compounds in Kishinev on September 21, 1963.

Studies of magnetic susceptibility showed that at the moment of melting it decreases by approximately 25–30%, and then, upon further heating of the melt, exhibits a certain tendency to increase.

On the basis of these data one may conclude that the group of A^{III}B^V compounds, like germanium and silicon (^{1–5}), passes upon melting into a metal-like state, i.e., according to A. R. Regel’s classification (³), these substances melt according to the semiconductor-metal type.

Studies of the electrical conductivity of zinc and cadmium tellurides (⁶) showed that at the moment of melting the electrical conductivity increases markedly (Table 1). It should be noted, however, that the electrical conductivity of melts of zinc and cadmium tellurides at the melting temperature is approximately 1.5–

2 orders of magnitude lower than the electrical conductivity of melts of $A^{III}B^V$ compounds at the melting temperature.

Heating melts of zinc and cadmium tellurides leads to an increase in electrical conductivity. Studies of magnetic susceptibility show the presence of a jump at the melting temperature (Table 1), which in absolute magnitude is considerably smaller than in $A^{III}B^V$ compounds and amounts to only 8-10%, indicating substantially smaller changes in the character of the chemical bond upon melting of the tellurides. Heating the melts leads to a noticeable decrease in magnetic susceptibility (⁷).

The data presented indicate the preservation of homeopolar bonds upon melting and that zinc and cadmium tellurides are semiconductors in the liquid state.

Thus, according to A. R. Regel's classification (³), zinc and cadmium tellurides pass from the solid to the liquid state according to the semiconductor-semiconductor type. Completely analogous changes are also observed upon melting gallium and indium tellurides (^{8,9}): Ga_2Te_3 and In_2Te_3 (see Table 1).

Studies of the electrical conductivity of the compound CuJ showed (¹⁰) that at the moment of melting the electrical conductivity increases somewhat (Table 1). It should be emphasized, however, that in absolute magnitude the electrical conductivity of a CuJ melt is approximately two orders of magnitude lower than that of $A^{III}\text{Te}$ compounds and four orders of magnitude lower than that of $A^{III}B^V$. These data indicate that, upon melting copper iodide, an ionic liquid is formed whose structural units are copper and iodine ions, Cu^+ and I^- .

Studies of the electrical conductivity and magnetic susceptibility of halides of the fourth group of the periodic system, which in the solid state have a NaCl-type lattice, gave the following results (see Table 1).

At the moment of melting the electrical conductivity increases discontinuously.

In the liquid-state region the electrical conductivity of the halides of the fourth group increases. The magnetic susceptibility upon melting of this group of compounds decreases noticeably (Table 1). The magnitude of the jump in magnetic susceptibility occupies an intermediate position between $A^{III}B^V$ compounds and the other investigated compounds with the ZnS lattice.

On the basis of the data obtained it may be concluded that the compounds with a NaCl-type lattice which we investigated, according to A. R. Regel's classification, melt according to the semiconductor-semiconductor type; moreover, while preserving their semiconducting nature in the liquid state, these compounds are distinguished by a fairly high level of electrical-conductivity values.

Studies of the electrical conductivity and magnetic susceptibility of compounds with a structure antizomorphic to the CaF_2 structure gave the following results, presented in Table 1.

At the moment of melting the electrical conductivity increases sharply, reaching, as in the case of $A^{III}B^V$ compounds, values of about $\sim 10\,000\text{ ohm}^{-1}\text{ cm}^{-1}$.

With increasing temperature, the electrical conductivity of melts of this group of compounds exhibits a certain tendency

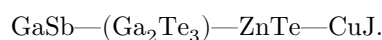
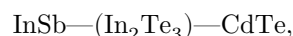
toward an increase. The magnetic susceptibility upon melting of compounds of this group decreases noticeably, and the magnitude of the jump decreases regularly in passing from Mg_2Si to Mg_2Pb .

Analysis of the results of studies of the electrical conductivity and magnetic susceptibility of semiconductor compounds of different structural groups makes it possible to draw the following conclusions.

A change in the metallic component of the bond in series of analogous compounds with “cationic” substitution does not affect the general character of the change in properties upon melting and subsequent heating, and consequently does not affect changes in the structure and character of the chemical bond. Examples of such series are: $\text{AlSb} \rightarrow \text{GaSb} \rightarrow \text{InSb}$, $\text{GeTe} \rightarrow \text{SnTe} \rightarrow \text{PbTe}$, etc.

In series of analogous compounds with “anionic” substitution, the ionic component of the bond also changes to a noticeable degree. Nevertheless, the character of the change in properties upon melting in compounds of these series is, in general, the same as in series of analogous compounds with cationic substitution. Examples of such series are: $\text{InSb} \rightarrow \text{InAs}$, $\text{PbTe} \rightarrow \text{PbSe} \rightarrow \text{PbS}$, $\text{Mg}_2\text{Si} \rightarrow \text{Mg}_2\text{Ge} \rightarrow \text{Mg}_2\text{Sn} \rightarrow \text{Mg}_2\text{Pb}$, etc.

A completely different regularity may be noted in isoelectronic series:



As was shown above, the first members of these series pass upon melting into a metal-like state (InSb , GaSb); the intermediate members retain covalent bonds upon melting and remain semiconductors (In_2Te_3 , Ga_2Te_3 , ZnTe , CdTe); while the last member of the isoelectronic series, belonging to the group of compounds of type $\text{A}^{\text{I}}\text{B}^{\text{VII}}$,—copper iodide—passes upon melting into an ionic liquid.*

Thus, compounds of isoelectronic series which in the solid state have a similar character of chemical bonding, the same structure, and practically completely identical interatomic distances and densities differ fundamentally from one another in the character of the change in their physicochemical properties upon melting.

However, this difference cannot be ascribed solely to the influence of the change in the ionic component of the bond, since $\text{A}^{\text{III}}\text{As}$ compounds differ significantly more in the difference of the electronegativities of the components from $\text{A}^{\text{III}}\text{Sb}$ compounds than do $\text{A}^{\text{II}}\text{Te}$ compounds, and nevertheless, judging from the change in properties upon melting and in the liquid state, $\text{A}^{\text{III}}\text{As}$ compounds,

like $A^{\text{III}}\text{Sb}$, are analogues, whereas the character of the change in the nature of the chemical bond and in the properties upon melting of $A^{\text{II}}\text{Te}$ compounds differs sharply.

Exactly the same conclusion can be drawn with regard to the influence of the initial structure in the solid state. Compounds of the groups $A^{\text{IIIB}}\text{V}$ and $A_2^{\text{IIB}}\text{IV}$ have substantially different structures in the solid state—respectively of the ZnS and CaF_2 types—yet upon melting their properties change in a completely analogous manner, and compounds of both these groups pass into a metal-like state. At the same time, within a single structural group, as already noted above, sharply different patterns of change in properties upon melting can be observed.

In connection with the foregoing, in our opinion the principal factor influencing the character of the change in properties upon melting of semiconductor compounds of different structural groups is the structure of the outer electron shells of the atoms forming the compounds.

* Incidentally, we note that this type of transition upon melting is absent in A. R. Regel's classification.

In doing so, one should proceed from the considerations set forth in the works of A. R. Regel and J. Bernal^(3,11), namely that the possibility of preserving homeopolar bonds during the melting of semiconductors is associated with the possibility of forming a chain or molecular structure that is stable under conditions of high mobility of the particles of the liquid. Analysis shows that, in the case of $A^{\text{III}}B^{\text{V}}$ compounds, the configuration of the outer electron shells of the components is such that, if homeopolar bonds are retained, only a spatial system of bonds is possible, with the formation of a mouse-trap-type structure with coordination number three. However, under conditions of high mobility of the particles of the liquid this is in principle impossible^(3,11). Therefore, as experiment also shows, upon melting $A^{\text{III}}B^{\text{V}}$ compounds a liquid with high coordination is formed, and some of the valence electrons pass into the electron gas. Obviously, an analogous conclusion can be drawn with respect to $A_2^{\text{II}}B^{\text{IV}}$ compounds. In the case of $A^{\text{II}}\text{Te}$ and $A^{\text{IV}}B^{\text{VI}}$ compounds, however, the configuration of the outer electron shells of the component atoms is such that there is a possibility of forming chain structures, as a result of which these compounds in the liquid state can retain homeopolar bonds and remain semiconductors. The data considered above on changes in properties upon melting of these compounds show that this is in fact observed.

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