The problem of intermediate valency

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The situation is found in a number of rare-earth compounds in which the narrow f level lies near the Fermi level, and configurations of the rare-earth ions differing in the number of f electrons (different valency) have close-lying energies. In this situation many properties of the corresponding substances, both thermodynamic (heat capacity, magnetic susceptibility, compressibility) and kinetic (optical properties, electric conductivity, etc.) are anomalous. Isostructural electronic phase transitions occur in these systems upon changing the external conditions. These are often simultaneously dielectric-metal and magnetic-nonmagnetic transitions. A phase having a narrow resonance level near E_F has been termed an intermediate-valence (IV) phase. This article reviews generally the problem of intermediate valency. The fundamental experimental facts are summarized. The conditions for appearance and the qualitative picture of IV states are discussed. A table is given of the currently know IV substances. The fundamental theoretical approaches to describing their properties and the electronic phase transitions in these systems are treated. The connection is established with other problems (the problem of dielectric-metal transitions, the Kondo effect, etc.). Major attention is paid to the fundamental unsolved problems.

CONTENTS

I. INTRODUCTION

As we know, the states of electrons in a solid are described by two limiting pictures. The usual band scheme, which is well applicable to most normal metals and semiconductors, starts with the picture of almost free electrons moving in the periodic field of the lattice. The corresponding states (Bloch waves) are delocalized; the interaction between the electrons is usually included in the Hartree-Fock approximation,

and it does not destroy the one-electron picture.

On the other hand, in a number of cases it is more adequate to describe the electrons in the language of localized states (this corresponds to the Heitler-London approximation in the theory of molecules). This approach is applicable when there is strong interelectronic correlation. Actually the electrons of the inner shells must be described in this way. Both approaches are fully equivalent for filled shells, but this is not

true for partly filled shells. In particular, some of the latter are the partly filled d and f states in the transition and rare-earth metals and in the actinides and their compounds. Owing to localization of the electrons, the corresponding substances generally prove to be magnetic: this often also involves the fact that many such compounds prove to be dielectrics (Mott dielectrics),[1,2] in contradiction to the predictions of band theory.

In compounds of the transition metals and actinides, the situation often proves intermediate between purely localized and collective states of the electrons. This is associated with especial difficulties in describing them theoretically. Yet the rare-earth metals and compounds that have been studied up to recent time have always manifested the case of extreme localization for the $4f$ electrons. Actually, the corresponding electron shells usually behave exactly like atomic shells: they have the same properties, and are characterized by the same quantum numbers L, S, and J as the states of the corresponding isolated ion. However, very recently a class of rare-earth compounds has been discovered and has attracted widespread attention in which the $4f$ shell, while in many ways keeping its atomlike character, has nevertheless lost its stability. These substances are characterized by the fact that states having different numbers of f electrons per center prove to lie close in energy (e.g., the states $4f^n$ and $4f^{n-1}$ + an electron in the conduction band). This resonance makes possible transitions between different configurations, the f electrons acquire a partial band character, and the mean number of f electrons per center (the valency of the ion) becomes nonintegral, etc. Compounds of this type have become termed intermediate-valency compounds.[1]

Intermediate-valency states (IVS) have a whole series of unique properties. For a change of external conditions (temperature, pressure, composition), they often undergo phase transitions of purely electronic nature involving a change in the filling of the electronic levels. As a rule, these transitions are isomorphous (without change in the lattice symmetry); in a number of cases they are dielectric-metal transitions. Simultaneously the magnetic properties usually change sharply (localized magnetic moments disappear). That is, these transitions are of the "magnetic-nonmagnetic state" type. Intermediate-valency states show sharp anomalies in practically any experimentally measurable characteristic: in lattice properties (anoma.ous compressibility), in heat capacity (anomalously large coefficient of linear heat capacity), in magnetic susceptibility, and in transport characteristics, especially in electric conductivity.

The fundamental problem in principle that we can hope to understand by studying this class of substances

(besides their intrinsic interest) is the relationship between the descriptions of the electrons in the language of localized and collective states: in which cases does the one or the other picture fit, how does the transition between them occur, and what peculiarities in the behavior of the system accompany this transition? Since the f electrons do in many ways retain their atomlike character, at least in certain respects the corresponding compounds seem at first glance simpler than the compounds of the d-metals and the actinides, for which generally all characteristic parameters prove to be of the order of unity. We can hope that an understanding of the situation with the IVS's can help in making sense with the properties of the transition metals and their compounds.

This review is concerned with a general treatment of the IV problem. It will not try to shed light on all details of this vigorously growing field nor on the whole variety of substances studied, their properties, and applied methods: The theme of the review lies rather in formulating the fundamental problems posed by study of IV systems (much concrete material is contained in the review articles[3-8,11] and in conference proceedings[9,10]).

Besides the general theoretical interest in the IV substances, they may also prove practically important. Attempts are already being made to employ the phase transition in SmS for optical recording and storage of information[3]; apparently these compounds may also prove promising in other fields. However, as Anderson[164] has noted, perhaps the most important fact is that most good catalysts are precisely intermediate-valence compounds (including the analogous compound of the transition metals). This can draw additional attention to these materials, not only from physicists, but also chemists, technologists, and specialists in catalysis.

2. CONDITIONS FOR APPEARANCE OF INTERMEDIATE VALENCY STATES AND A QUALITATIVE PICTURE OF THEM

As we have noted, the fundamental features of IV phases involve the fact that states differing in occupancy of electronic orbitals prove to lie close in energy, e.g., the states $4f^n$ and $4f^{n-1} + (sd)$ (the electron leaving the f level occupies one of the states in the conduction band, usually one of d character). The possibility of this resonance essentially arises from the very nature of the $4f$ electrons, whose energy levels in the atom are close to the $5d$ and $6s$ levels. Of course, exact resonance in an isolated atom or ion is highly improbable. However, in a solid in which the outer $5d$ and $6s$ levels are spread out into rather broad bands, the conditions for this are substantially facilitated. Currently we know rather many compounds in which such a situation is realized (see Table II, p.).

First let us examine the situations in which an IVS arises. Usually the rare-earth elements are trivalent, both as the pure metals and in compounds (i.e., their ion core is R^{3+}). However, a number of them can

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[1] The terminology in this field has not yet fully stabilized. The corresponding states are called mixed-valency (MV) states, intermediate-valency states, and states with interconfigurational fluctuations (ICF).

TABLE I. Configurations of ions forming intermediate-valency compounds.

Ion	Ce^{4+}	Ce^{3+}	Sm^{2+}	Sm^{3+}	Eu^{2+}	Eu^{3+}	Tm^{2+}	Tm^{3+}	Yb^{2+}	Yb^{3+}
Occupation of shell	$4f^0$	$4f^1$	$4f^6$	$4f^5$	$4f^7$	$4f^6$	$4f^{13}$	$4f^{12}$	$4f^{14}$	$4f^{13}$
Term	$^1S_0$	$^2F_{5/2}$	$^7F_0$	$^6H_{5/2}$	$^8S_{7/2}$	$^7F_0$	$^2F_{7/2}$	$^3H_6$	$^1S_0$	$^2F_{7/2}$

possess an anomalous valency (2 or 4). This involves the especial stability of completely filled or empty as well as half-filled atomic shells. Consequently anomalous valency is shown by the elements at the beginning (Ce), in the middle (Sm, Eu) and at the end (Tm, Yb) of the $4f$ period. Table I gives the electronic configurations of the corresponding ions.

For example, actually cerium proves tetravalent in a number of compounds (in this state its $4f$ shell is empty). Moreover, pure metallic cerium undergoes an electronic phase transition from the state Ce^{3+} to a state of higher valency (smaller number of f electrons per center) under pressure or upon addition, e.g., of thorium.[12] However, the transition does not lead to the state $Ce^{4+}(4f^0)$ but to an IV state ($\sim Ce^{+3.7}$). Here the Ce^{3+} ions possess a magnetic moment ($S = 1/2$, $J = 5/2$), while the Ce^{4+} ion is nonmagnetic. An analogous magnetic-nonmagnetic transition of Ce is observed, e.g., for admixture of Ce in La[52] under pressure and in various other matrices. IVS's with anomalous properties have been detected in many alloys and compounds of cerium (see Table II).

An analogous situation occurs also in many compounds of the other rare-earth elements at the ends and in the middle of the period. We can illustrate this with the example of the chalcogenides of the rare-earth metals. Figure 1 shows the lattice parameters of the series of these compounds. In com-

TABLE II. Intermediate-valency compounds.

(a) Intermediate-valency states under normal conditions.

Substance	Reference	Substance	Reference	Substance	Reference
Ce $(T > 100 K)$	13, 55	Sm_3S_4 b)	20, 21, 34	$YbAl_2$	11
$CePd_3$	13	Sm_4Bi_3	22, 116	$YbAl_3$	31
CeN	7, 14, 63	Sm_4Sb_3 c)	22	$YbCu$	17, 31
$CeSn_3$	7	$EuRh_2$	33	$YbCu_2$	7
$CeAl_2$ a)d)	15, 64, 67	$EuIr_2$	162	$YbIn_3$	7
$CeAl_3$ a)	15, 16, 65	$EuPt_2$ f)	163	$YbAu$	31
$CeFe_2$	4	$EuZn_2$	32	$YbZn$	32
$CeCo_2$ e)	4	Eu_3S_4 b)	21, 25, 34	Yb_4Bi_3 c)	32
$CoNi_2$	4	Eu_3Sb_3 c)	22	Yb_4Sb_3 c)	32
$CeNi_5$	17	$EuCu_2Si_2$	26	$YbCu_2Si_2$	31
$CeCu_2Si_2$	7	EuM_2Si_2 h),	177	$YbCuAl$	149
$CeAg_2$	165	M=Fe, Co, Ni		$YbInAu_2$	33
CeAs	166	$TmSe$ d)	27—29	$YbNi_2Ge_2$	33
$CeBe_{13}$	176	$TmZn_2$ d)	30	$YbAu_2$ g)	165
Sm g)	178	YbC_2	31	$YbBe_{13}$	176
SmB_6	18, 19	YbB_4	31		

Notes: a) Known as systems showing the Kondo effect.[59] The valency of Ce is apparently very close to three. b) Inhomogeneous mixed valency (thermally activated hopping between the states R^{2+} and R^{3+}). c) Type of IV not exactly established. d) Magnetically ordered state at low temperatures.[148,30] e) Superconducting state at low temperatures.[44,66] f) Existence of an IV not exactly proven.[163] g) IV state at the surface. h) Apparently an inhomogeneous IV.

(b) Doped compounds and alloys.

Compound	Reference	Compound	Reference
$Ce_{1-x}Th_x$ a)	35	$Sm_{1-x}Yb_xS$ c)	36
$La_{1-x}Ce_xPd_3$	7	$Sm_{1-x}Th_xS$	7
$Ce(Rh_{1-x}Pd_x)_3$	7	$SmS_{1-x}As_x$	9
$Ce(Ni_{1-x}Cu_x)_5$	17	$SmSb_xS_{1-x}$	151
$CeIn_{3-x}Sn_x$	75	$Sm_{1-x}La_xB_6$	152
$Ce_{0.9-x}M_xTh_{0.1}$,	179	$EuNi_{5-x}Cu_x$	42
M = various rare-earth ions		$EuRh_{2-x}Pt_x$	23
$Ce_{1-x}M_xAl_2$, M=Y, Sc, Eu, Th	180	$Eu_{1-x}La_xRh_2$	41, 43
$CeRu_2H_x$ d)	181	$EuIr_{2-x}Pt_x$	42, 43
$Sm_{1-x}Gd_xS$ b)	36	$TmSe_{0.83}Te_{0.17}$ e)	183
$Sm_{1-x}R_x^{3+}S$,	3, 4, 6	$Yb(Ni_{1-x}Cu_x)_5$	17
R = almost all trivalent rare-earth metals		$YbNi_{1-x}Cu_x$	17
$Sm_{1-x}Eu_xS$ c)	4, 37	$Yb_{1-x}Sc_xAl_2$	150

Notes: a) The phase-transition line in the x, T plane ends at the critical point $x^* = 0.265$, $T^* = 148$ K, b) complex phase diagram (see Fig. 7). c) Existence of an IV questioned. Many data are interpreted as contradicting an IV.[6,8] However, according to the data of Refs. 4, 37, 38, the valency of Sm in these compounds is fractional; see also Ref. 39. d) The valency of Ce varies from +4 to +3 with x increasing from 0 to 4; the data for intermediate values of x are not given. e) Spontaneous magnetization exists at $T = 0$ in the absence of an external magnetic field.

(c) Transitions to an intermediate-valency state under pressure.

Substance	Transition pressure, kbar ($T = 300$ K)	Character of transition ($T = 300$ K) I—first-order transition II—continuous transition	Reference	Substance	Transition pressure, kbar ($T = 300$K)	Character of transition ($T = 300$ K) I—first-order transition II—continuous transition	Reference
Ce, $\gamma - \alpha$ a)	7	I	12	SmSe	40	II	47
Ce, $\alpha - \alpha'$ b)	40	I	12, 44	SmTe	50	II	47
$CeAl_2$	65	I	50, 174	$SmS_{1-x}Se_x$	7—40	I for $x < 0.8$ II for $x > 0.8$	48
CeP	100		68				
CeS	120		175				
SmS c)	6.5	I	3, 6	Sm_4Bi_3 d)	26	I	115
$Sm_{0.8}Yb_{0.2}S$	7.5	I	46	EuO	300	I	47
$Sm_{0.8}Eu_{0.2}S$	15	I	46	TmTe e)	20—30	II	49
$Sm_{0.8}Ca_{0.2}S$	12.4	I	46	YbS	150—200	II	47
$Sm_{0.7}Ca_{0.3}S$	$\geqslant 15$	II	46	YbSe	150—200	II	47
				YbTe	150—200	II	47

Notes: a) Ends at the critical point $P^* = 18$ kbar, $T^* = 550$ K.[58,51] b) The crystal structure of the α' phase has not been finally clarified; it may be a mixture of phases α' and α''.[44] c) Apparently ends at the critical point $P^* = 7$ kbar, $T^* = 700$ K[6,45]; perhaps there is another transition at $P \approx 20$ kbar.[40] d) Sm_4Bi_3 has an IV even at $P = 0$; it is not yet clear whether the transition at 26 kbar is a transition to a different IV phase or to a phase with the integral valency Sm^{3+}. e) According to the data of Ref. 49, there are apparently two successive transitions at low temperatures at $P_1 \approx 30$ kbar and $P_2 \approx 40$ kbar.

pounds of the type $R^{3+}X$, we see that the chalcogenides of Eu, Sm, Yb, and in part Tm, show anomalously large interatomic distances on the background of the smooth variation of the lattice parameters ("lanthanide contraction"). This is explained precisely by the fact that the rare-earth ions in them exist in the state R^{2+} (or close to it). The corresponding ion has a larger ionic radius, which is manifested in the increased lattice parameter. Let us say directly that measurements of the lattice parameter usually serve
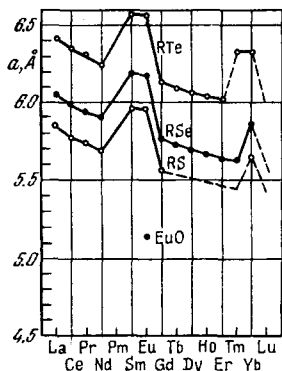
FIG. 1. Lattice parameters of rare-earth chalcogenides.

as the simplest method of determining the mean valency of a compound and detecting an IVS: the appearance of a state with a lattice parameter intermediate between the value characteristic of substances having an integral valency indicates the appearance of an IVS, while the mean number of f electrons per center is determined from the lattice parameter by linear interpolation.

Turning to the energy pattern, we can represent the behavior of the IVS's by the following diagram (Fig. 2). It shows the ordinary conduction band, and in the same diagram the level of a single (outer) f electron is drawn[2] (for simplicity we neglect the splitting of levels corresponding to different L, S, J terms and their splitting by the crystal field). The state of Fig. 2a corresponds to the initial integral valency (let it be the state R^{2+}). Upon applying, say, external pressure, the relative arrangement of the terms is altered (e.g., by broadening of the d band or increase of the splitting of the e_g and t_{2g}-subbands of the d band). Thus a transition can occur to states of the type of Fig. 2b, and then of Fig. 2c. In this case Fig. 2b corresponds to an IV phase; Fig. 2c now describes the integral-valency state R^{3+}. The transitions between these states can be either continuous or discontinuous (see Chap. 3 for more details). Thus an IVS corresponds to a position of the f level near the Fermi level E_f; the fundamental anomalous properties of these compounds are precisely associated with the existence of an extremely narrow resonance level directly at the Fermi surface.

Here we can speak of the electronic phase transition (EPT) itself in several equivalent ways. We can speak of a transition between different electronic configurations caused by crossing of the corresponding energy levels. We can treat it also as the transition of an electron from a localized f level to the conduction band; this same transition corresponds simultaneously to a change in the number of f electrons per ion, i.e.,

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[2] Strictly speaking, the corresponding level is a many-electron level, and it is not quite correct to draw it in a single-electron energy diagram. Nevertheless, one can employ this picture, while recalling that the states corresponding to the f level are localized, and the Coulombic repulsion of the f electrons makes a substantial contribution to their energy, with the result that only one electron can be placed in such a level, rather than two, as in an ordinary level in a band.[2]
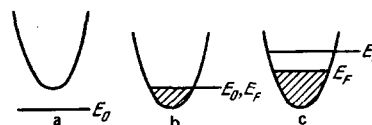
FIG. 2. Schematic of the energy diagram of states of integral (a, c) and intermediate (b) valency.

to a valency change. The various terms employed, which were mentioned in the Introduction, involve these different approaches and emphasize some particular aspect of the phenomenon at hand.

Let us immediately discuss another aspect. The possibility of transitions between the configurations $4f^n$ and $4f^{n-1} + (sd)$ causes the exact wave functions to be superpositions of f and (sd) states. That is, the f electrons seem to become partly delocalized (for an isolated rare-earth admixture in a metal, this leads to a finite width Γ of the f level[53,54]). It is qualitatively evident that IVS's are realized when the following condition is satisfied:

$$|E_{ex}| = |E^n - E^{n-1, sd}| \lesssim \Gamma. \tag{1}$$

The existence of a finite width (or damping) of the f levels determines in many ways the behavior and properties of the system in an IVS phase. Before we proceed to discuss them, however, we shall examine how the transition with valency change itself occurs.

3. ELECTRONIC PHASE TRANSITIONS WITH VALENCY CHANGE

a) The experimental situation

Isomorphous phase transitions caused by change in the electronic structure have been found in a number of rare-earth compounds. The best studied transitions are those in cerium and in the chalcogenides of samarium.

1) *Cerium.* The existence of a series of phases has been established in Ce (Fig. 3).[12] Of interest to us are the γ, α, and α' phases. The γ and α phases have a face-centered cubic structure; a first-order transition between them occurs at room temperature at a pressure $P = 7.5$ kbar with considerable hysteresis. In the γ phase cerium is practically trivalent, as is implied by the values of the lattice parameter (Fig. 4) and the magnetic susceptibility (existence of a magnetic moment corresponding to the term $4f^1\,{}^2F_{5/2}$). The phase
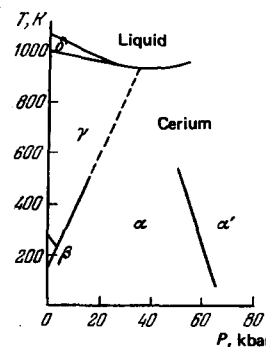

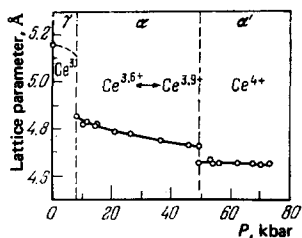
FIG. 3. Phase diagram of cerium.[12]

FIG. 4. Pressure-dependence of the lattice parameter of Ce.[56]

transition is accompanied by an abrupt volume change of ~15%. Here the magnetic properties, resistance, thermo-emf, etc., are sharply altered.[55] However, the α phase does not correspond to an integral valency; the lattice parameter and other data show that the valency of Ce in the α phase in the immediate vicinity of the transition amounts to ~3.67. The occupancy of the f level continues to decline with further increase in pressure to the value ~3.85. Then at $P \approx 40$ kbar a phase transition occurs again to the new phase α', which now has a valency ≈ 4. In the α phase, in spite of the nominal presence of a certain number of f electrons, there are no localized magnetic moments and no magnetic ordering has been found as $T \to 0$. Near the $\alpha - \alpha'$ transition boundary, the α phase is a superconductor, though with extremely low values of the critical temperature $T_c \approx 20-40$ mK.[44] The α' phase is a superconductor with $T_c \approx 1.5-2$ K.[44] The literature contains contradictory data on its crystal structure: the first publications reported that the α' phase, like the γ and α phases, has a fcc structure.[56] However, later its structure was determined as a distorted hcp or as an $\alpha - U$ structure.[57] Here the coexistence of different phases was observed at $P \gtrsim 51$ kbar. However, in any case the deviation from fcc structure is small.

The $\gamma - \alpha$ phase equilibrium line has a positive slope and ends at the critical point $T^* = 550$ K, $P^* = 18$ kbar.[58,51] It extrapolates at high temperatures into the region of the minimum on the melting curve. Apparently the very existence of the latter involves electronic rearrangement, which probably occurs also in the liquid phase.[51] Very little is known about the nature of the $\alpha - \alpha'$ phase equilibrium line. Apparently it also extrapolates into the region of the minimum on the melting curve. However, this has not been established exactly, nor whether a critical point occurs on it.

Cerium is a metal even in the γ phase. Its energy diagram is shown schematically in Fig. 5 (which shows an f level of finite width). Hence the ETP in Ce is a metal-metal transition. The electronic structure of the other class of compounds that has been studied in detail (the chalcogenides of samarium) is analogous to
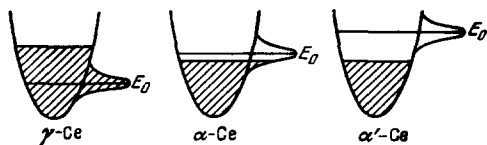
that shown in Fig. 2, and the corresponding transition in them is at the same time a dielectric-metal transition.

2) *Rare-earth chalcogenides*.[3,6,8] Under normal conditions samarium sulfide SmS is a semiconductor with a narrow forbidden band $E_g \approx 0.06-0.25$ eV, in which samarium is bivalent (cf. Fig. 1). A first-order transition occurs in it at 6.5 kbar pressure with a jump in volume, while the NaCl-type structure is maintained. The conductivity rises in the transition by a factor of 7–10 (Fig. 6): Hall-effect data imply that the mobility of the electrons declines in the transition by a factor of approximately 20, so that actually the carrier concentration rises in the transition by a factor of about 10^2 and becomes of the order of 10^{22} cm^{-3}.[60]

The transition is manifested most strikingly in the optical properties (appearance of a plasma edge in reflection). This can be seen directly from the change in color of the specimen (transition from the black semiconductor modification to a lustrous, "golden" metal).

In analogy to the case of Ce, the phase equilibrium line in SmS at high temperatures also has a positive slope. Apparently it terminates in a critical point with the coordinates $T^* = 1000$ K, $P^* = 7$ kbar.[45] The slope of the phase equilibrium line at low temperatures is not exactly known; there are indications that in this region $dT_c/dP < 0$.[61,62,76]

Dielectric-metal transitions are also observed in SmSe and SmTe (see Fig. 6); they are also manifested most strikingly in the optical properties. At room temperature, at which the measurements were performed, the transitions in these substances are continuous. It is not clear at present whether this is generally inherent in these compounds, or whether a first-order transition will still occur in them at low enough temperatures, but with a low-lying critical point, so that room temperature already proves supercritical for them.

The transitions in the samarium chalcogenides are due to change in valency of Sm and partial transition of an f electron to the conduction band. After the transition these compounds also prove to be in an IV phase. In SmS the valency of Sm near the transition is
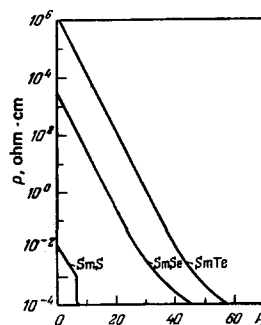

FIG. 5. Schematic of the energy spectrum of Ce in different phases. Occupied states are cross-hatched.

FIG. 6. Pressure-dependence of the conductivity of samarium chalcogenides ($T = 300$ K).[6]

~+2.7 and increases smoothly with further pressure increase. Just like the α phase of Ce, this phase has a whole set of anomalous properties that will be treated in Chap. 4. Recently indications[40] have appeared that perhaps in SmS, just as in Ce, yet another phase exists at high pressures ($P \gtrsim 20$ kbar). The problem of the overall form of the phase diagram for SmS is thus still open.

Let us briefly discuss several further examples of compounds in which EPTs have been found. The bivalent state of europium is more stable than in samarium. Yet at high enough pressures a transition with change of valency can also occur in Eu compounds. Thus far the corresponding transition has been found only in EuO at the pressure $P \approx 150$ kbar.[47] An analogous situation occurs in the chalcogenides of ytterbium (see Table II).

In the chalcogenides of thulium, where the bivalent state is less stable, it turns out that at normal pressure Tm is bivalent in TmTe, trivalent in TmS, and has an IV in TmSe (see, e.g., Ref. 29). Here the valency in both TmSe and in TmTe varies under pressure.[49]

The thulium compounds differ from all the rest of the IV compounds in that Tm proves magnetic in both configurations (if the possible role of the crystal field is neglected); see Table I. Hence they show magnetic ordering at low temperatures, so that interesting effects are observed under the action of a magnetic field, etc.[77-79]

3) *Transitions with change of composition of a compound.* Besides the pressure and the temperature, another possibility of changing the valency and inducing a transition involves changing the composition of a compound. Thus, one can shift the $\gamma - \alpha$ phase-transition line in Ce (see Fig. 3) to the left by adding thorium; in the alloy $Ce_{1-x}Th_x$ at the value $x^* = 0.265$, the critical point lies in the region $P^* = 0$, $T^* = 148$ K,[35] which substantially facilitates study of the critical behavior of this system. This study, which has been performed by Parks', group has yielded a number of interesting results.[35,69]

Analogously, a transition with valency change can be induced in SmS by adding to it many rare-earth ions (Y, Gd, Nd, etc.) and Th.[6] Figure 7 shows the corresponding phase diagram for the system $Sm_{1-x}Gd_xS$.[36]
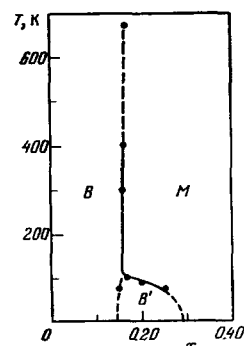
A number of questions arise in examining such systems. The major one involves the mechanism of the effect of the admixtures. It was initially thought that the transition is caused by impurities that have a smaller radius than that of the Sm^{2+} ion. In this case their action is simply equivalent to the action of external pressure ("internal compression"). However, a set of data has forced a change of this viewpoint. To judge from the lattice parameter, the optical properties, and the resistivity, in the systems $Sm_{1-x}Yb_xS$ and $Sm_{1-x}Ca_xS$, no transition with valency change occurs at any values of x,[6] despite the fact that the ions Yb^{2+} and Ca^{2+} have a considerably smaller ionic radius than Sm^{2+}. They concluded from this that the major factor that affects the transition is the electronic structure: if to SmS we add, e.g., GdS, a substance that *per se* is metallic in character and contains Gd^{3+} ions, then a corresponding transition of the f electrons into the condition band is also induced in the Sm ions. Yet in alloys of the type $Sm_{1-x}R_x^{2+}S$ in which *per se* the compound $R^{2+}S$ (CaS, YbS) is a semiconductor with a rather wide forbidden band, such a transition does not occur, and the alloy remains a semiconductor for all x, in spite of the smaller radius of the Ca^{2+} and Yb^{2+} ions as compared with the radius of Sm^{2+}.

However, there are experimental data that contradict this picture. These alloys were studied by measuring the chemical shifts of x-ray lines[4] as well as x-ray absorption spectra[37] (this allows one directly to study the electronic configuration of the ion, i.e., the valency of the individual components of the alloy). Here it was established that a gradual Sm^{2+}-Sm^{3+} transition occurs in both $Sm_{1-x}Eu_xS$[4,37] and in $Sm_{1-x}Yb_xS$[38] with increasing x (Fig. 8). A possible explanation of this experimental contradiction might consist in the following.[4,39] We can assume that an individual Sm impurity, say in EuS, exists in the state Sm^{3+}. The f electron from Sm here goes to a corresponding level of Eu (in the d band) rather than to the d band of Sm itself,
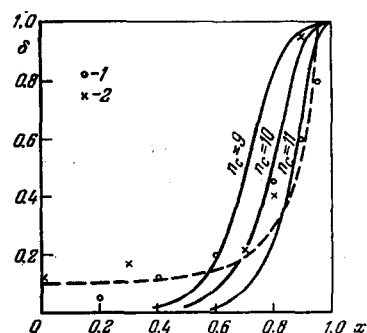

FIG. 8. Mean valency of $Sm^{(2+\delta)+}$ (ion fraction Sm^{3+}/Sm) in the system $Sm_{1-x}Eu_xS$, 1—data of Ref. 37, 2—data of Refs. 73, 4. The solid lines[39] show the relationship $P(x) = \sum_{n=n_c}^{12} C_{12}^n x^n (1-x)^{12-n}$ derived under the assumption that the Sm ion exists in the state Sm^{3+} if the number of "foreign" nearest neighbors R^{2+} around it is greater than a certain critical value $n > n_c$, and in the form Sm^{2+} for $n < n_c$. The dotted line is the variation of the mean valency according to Eqs. (11) and (12)[39] (the values of the parameters are taken as $V = 0.5$ eV, $E_g(0) = 0.2$ eV, the mass in the conduction band equals the mass of a free electron, and the f level is shifted upward linearly with varying x).

FIG. 7. Phase diagram of $Sm_{1-x}Gd_xS$.[36]

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while remaining bound near the donor Sm^{3+}. If the concentration of such centers is small, and less than the critical concentration for production of an impurity band or the percolation threshold, then the material remains a semiconductor. At the same time, the methods that directly measure the electronic configuration of the individual Sm ions (e.g., sutdy of x-ray spectra) will reveal Sm^{3+} ions. Simple estimates[39] starting with this model reasonably describe the change of valency of Sm in $Sm_{1-x}Eu_xS$ (see Fig. 8). The fundamental assumption here is that the bottom of the conduction band of EuS lies lower than the f level of Sm. The lowering of the bottom of the t_{2g} band of EuS with respect to SmS is implied by the energy diagram of Wilson.[74] It is as yet unclear whether it suffices to induce a Sm^{2+}-Sm^{3+} transition (it would have to amount to ≥ 0.2 eV to do this). It is also not yet fully clear how to explain on this picture the increase in the transition pressure in systems of the type of $Sm_{1-x}R_x^{2+}S$ as compared with SmS[46] (see Table II, c)[3'], as well as the slight change in optical properties and the behavior of the lattice parameter with varying x.[8] However, on the whole it seems quite plausible.

A second interesting problem involves the form of the phase diagram for systems of the type $Sm_{1-x}Gd_xS$ (see Fig. 7). First of all, it is not clear whether the phase B' is a special phase[36,71] or is identical with the original semiconductor B phase of SmS.[72] If the B' phase is a special phase different from B, then we must ascertain precisely in what this difference lies, why the B' phase proves to exist at lower temperature than the metallic phase M (the slope of the phase equilibrium line $B-M$ is positive), and also why the $M-B'$ transition in $Sm_{1-x}Gd_xS$ proves to be so sharp.[36] Wilson's study[74] associates the existence of the B' phase with the role of disorder, and the $M-B'$ transition with a Mott-Anderson transition; an important role of lattice effects in this transition is also possible.[5] Apparently the phase diagram of pure SmS (see above) also has a similar "recurrent" nature. Theoretical discussions on the form of the phase diagram for IV systems are given in Chap. 3, Sec. b, 6.

We note again that an entire set of substances (see Table II) exhibit an IVS even under normal conditions, and a transition with valency change has not been discovered in them.

b) Theoretical treatment of electronic phase transitions

1) *Formulation of the problem*. When one attempts a theoretical treatment of EPTs, first of all, the same sort of problems arise as in discussing any other phase transitions in a solid: what are the fundamental factors, the mechanisms responsible for the transition, how do they govern its characteristics, when does the transition prove to be discontinuous, and when continuous, etc. However, yet another very specific and fundamental problem arises in the systems studied. As we have seen in Sec. a, an IVS usually arises near

the transition in EPTs in rare-earth compounds. This practically always happens, and there is apparently not a single example of a transition directly between states of integral valency. Why this happens and what factors fix the f level near the Fermi level and stabilize the IVS is one of the fundamental questions in the entire problem of intermediate valency. In presenting below the various theoretical approaches to describing EPTs, we shall pay especial attention to this question.

We note immediately that IVSs naturally appear in the simplest approximation with noninteracting electrons, even when we neglect the broadening of the f level. Actually, let us examine the situation shown in Fig. 2, a-c. We shall take the bottom of the conduction band as the energy origin and denote the position of the f level as E_0. Evidently, as long as $E_0 < 0$, the number of f electrons is integral (everywhere from now on we shall speak only of the filling of the upper or last f level; correspondingly the number of f electrons per center n_f can vary from 1 to 0). When the f level overlaps the bottom of the conduction band, part of the f electrons will go to states in the conduction band having energies $\varepsilon_k < E_0$. While the number of states per center is $n_s < 1$, the Fermi level automatically coincides with the position E_0 of the f level, and the substance exists in an IV phase ($n_s < 1, 0 < n_f < 1, n_s + n_f = 1$). When the f level rises high enough, so that the states with $_k < E_0$ contain all the f electrons, E_0 detaches from E_F, and the valency again becomes integral, differing by unity from the original value. The character of the dependence of the number of f electrons per center on the position of the f level in this case is shown schematically below (see Fig. 10a).

However, in this simplest approximation the EPT always proves continuous. This is not surprising, since no interactions have been taken into account here. In the systems studied the most substantial interactions prove to be the Coulombic interaction of the electrons (especially the f electrons and the conduction electrons—for the sake of simplicity, we shall call them s electrons), as well as the interaction of the electrons with the lattice. Accordingly, two approaches have developed for describing EPTs. We shall now proceed to examine them.

2) *Electron-electron interactions (the Falicov-Kimball model)*. One of the first factors adduced for describing the features of EPTs in rare-earth compounds has been the inclusion of Coulomb interaction of the f and s electrons.[80,81] In the simplest variant, this interaction has been replaced by a short-range interaction. The Hamiltonian of this model has the following form (for simplicity we are still neglecting the spins of the electrons):

$$H = \sum_k \varepsilon_k a_k^+ a_k + E_0 \sum_m c_m^+ c_m + \frac{G}{N} \sum_{k, k', m} a_k^+ a_{k'} c_m^+ c_m. \qquad (2)$$

Here a_k^+ and c_m^+ are respectively the operators for creation of an s electron of momentum k and of an f electron at the node m.

In the self-consistent-field (SCF) approximation, if we represent the last term in (2) in the form $G n_f n_s$

[3']This can be explained partly by the lesser compressibility of these compounds as compared with SmS.[46]

$=G(1-n_s)n_s$, we can easily write the energy of the system as a function of the number of electrons $n_s = 1 - n_f$ that have gone from the f level into the conduction band. If we take the density of states in the s band as constant, $\rho(\varepsilon) = \rho = \text{const}$, then we get

$$\mathscr{E} = \langle\mathscr{H}\rangle = E_g n_s + \frac{1}{2\rho} n_s^2 - G n_s^2, \quad E_g = G - E_0. \tag{3}$$

This expression holds for systems of the type of Ce. For substances of the type of SmS, where the f level overlaps the bottom of the conduction band, it is more correct to take $\rho(\varepsilon) \sim W^{-3/2}\sqrt{\varepsilon}$ (W is a quantity of the order of the width of the conduction band). In this case the contribution to the energy from the kinetic energy of the s electrons occupying the lower states of the s band will differ, and instead of (3) we get the following expression[48,4]

$$\mathscr{E} = E_g n_s + C W n_s^{5/3} - G n_s^2 \tag{4}$$

(C is a numerical constant ~1). The qualitative conclusions from this do not change substantially; they consist in the following. As we see from (3) and (4), as E_0 increases, either a discontinuous transition can occur from the state with $n_s \leqslant 0$ ($n_f = 1$) to $n_s = 1$ (for $G > 1/2\rho$ in (3)), or the transition can be continuous (see Fig. 9a, which shows the dependence of the energy $\mathscr{E}$ on the number n_s of s electrons in the band when $G > 1/2\rho$ and for various values of E_g). In the case of (4), the situation is somewhat more complicated, and in principle discontinuous transitions can occur from a state with $0 < n_s < 1$ to $n_s = 1$ (Fig. 9b). Correspondingly, the dependence of the number of f electrons on the position E_0 of the f level is shown schematically in Fig. 10 (Fig. 10a is the case of noninteracting electrons).

One can perform an analogous treatment in the SCF approximation and at finite temperature.[81] It turns out that the jump in n_f decreases with increasing temperature and vanishes at some critical value (T^*, E_0^*), which the authors have correlated with the critical point for the $\gamma - \alpha$ transition in Ce. The slope of the phase equilibrium curve in the $E_0 - T$ plane in the treatment of Ref. 81 is determined mainly by the spin entropy of the corresponding phases.

Thus, the Falicov model presented here can explain the existence of a first-order transition that terminates at a critical point, and gives certain indications of the possible form of the phase diagram of the system. It is also explains qualitatively why the interaction of the f and s electrons leads to a discontinuous EPT.

Suppose the f level lies below the Fermi level (or the bottom of the conduction band), $E_0 < 0$, and let it be filled, $n_f = 1$. Excitation of a fraction n_s of the f electrons to the conduction band requires expending the energy $(-E_0)n_s$ plus the kinetic energy for displacing n_s electrons into the conduction band. This energy loss is reflected by the first two terms in (3) and (4). However, in this excitation we gain in the
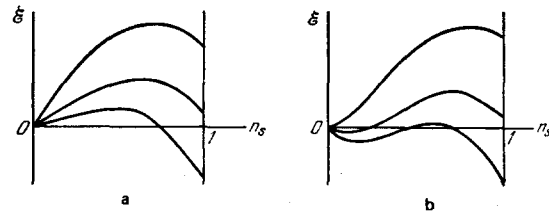
energy of attraction of the s electrons to the f holes. The SCF approximation, corresponds to the situation in which both the f electrons (or f holes with concentration $1 - n_f = n_s$) and the s electrons are assumed to be uniformly diffused in space. Then this gain proves to be quadratic in the concentration of excitations $-G n_s^2$. This favors a discontinuous transition directly to a state of integral valency, $n_s = 1$, $n_f = 0$ beginning at some value of E_0. Yet actually, as we have noted, an IVS is generally realized after the transition, rather than such a state. This is one of the essential defects of the original treatment of Refs. 80 and 81.

One of the first and most natural ways out of this complication was to take account of hybridization of the f and s electrons. This has been done in Refs. 82 and 83; later, analogous results have been obtained also in Refs. 84–86. The complete Hamiltonian of the model including hybridization takes the following form[5]:

$$H = \sum_{k\sigma} \varepsilon_k a_{k\sigma}^+ a_{k\sigma} + E_0 \sum_{m\sigma} c_{m\sigma}^+ c_{m\sigma} + \frac{U}{2} \sum_{m\sigma} c_{m\sigma}^+ c_{m\sigma} c_{m-\sigma}^+ c_{m-\sigma}$$
$$+ \frac{1}{\sqrt{N}} \sum_{km\sigma} (V_{km} a_{k\sigma}^+ c_{m\sigma} + \text{h.c.}) + \frac{1}{N} \sum_{\substack{kk'm \\ \sigma\sigma'}} G_{kk'm} a_{k\sigma}^+ a_{k'\sigma} c_{m\sigma'}^+ c_{m\sigma'}. \tag{5}$$

In this expression we can easily recognize Anderson's model[88] generalized to the case of many f centers and with additional inclusion of direct Coulombic interaction of the f and s electrons. Here the lattice periodicity is taken into account by the choice of hybridization matrix element in the form $V_{km} = V_k e^{i k \cdot R_m}$, and analogously in the term for the $f - s$ interaction. However, the effects of periodicity in the Hamiltonian of (5) are often not taken into account. This is equivalent to treating the rare-earth compound
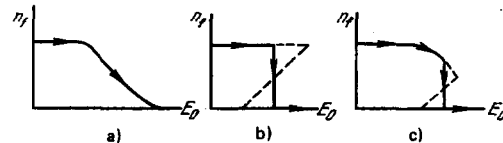

FIG. 9. Dependence of the energy on the occupation of the f level $n_f = 1 - n_s$ for different values of the energy E_0 of the f level. a) According to Eq. (3); b) according to Eq. (4).

FIG. 10. Dependence of the occupation nf of the f level on its position E_0 in the Falicov model. a) Noninteracting electrons; b) constant density of states ρ, strong interaction (see Eq. (3)); c) $\rho(\varepsilon) \sim \sqrt{\varepsilon}$, strong interaction (see Eq. (4)).

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[4] Eqs. (3) and (4) hold for the simple model of (2); in the general case the energy should contain exchange and correlation terms (see below, Sec. 4).

[5] We have explicitly also included the Coulombic repulsion of the f electrons at a center, which did not figure in the spin-free model; it is large for the f electrons, $U \approx 5-7$ eV.[5,87]

as an assembly of "rare-earth impurities" lying at all the lattice sites, but behaving independently and incoherently. Owing to the small radius of the f shell and the strong interelectronic correlation, the different f centers are actually incoherent, except at the lowest temperatures. It turns out that many of the features of the IV phenomenon can be understood with this "impurity" model, which we have actually already employed used in our qualitative discussion (in this regard, see also Ref. 89). The problem of establishing coherence in these systems is actually one of principle, and lies at the center of the entire IV problem, ultimately determining the structure and properties of the ground state of the system. These problems will be discussed in Chap. 4, and in the meantime we shall often employ the "impurity" model. The details of the conclusion involving this approximation will be especially noted at the appropriate places.

The model of (5) is easily studied in the SCF approximation. Let us first give the results for the simplest case of spinless particles. This variant imitates the case of strong $f-f$ interaction $U \to \infty$. We shall treat the "impurity" model with $V_{km} = V$, and $G_{kk'm} = G$.[83] In this case we can easily find the expression for the Green's function of the f electrons:

$$G_f(\omega) = \langle\langle c_m | c_m^+ \rangle\rangle = \frac{1}{2\pi} \frac{1}{\omega - E_0 - Gn_s - \Sigma(\omega)}, \qquad (6)$$

$$\Sigma(\omega) = \frac{1}{N} \sum_k \frac{V^2}{\omega - \varepsilon_k - Gn_f}. \qquad (7)$$

The difference from Anderson's treatment[88] actually consists here only in the appearance of the level shifts Gn_s and Gn_f.

Let us neglect, as usual,[88] the real part of $\Sigma(\omega)$, which gives the level shift (this is valid for the case shown in Fig. 5, and generally false for systems of the SmS type, where the f level lies near the edge of the conduction band). Then we get from (6) and (7) the density of states of f electrons in the form

$$\rho_f(\omega) = \frac{1}{\pi} \frac{\Gamma}{(\omega - E_0 - Gn_s)^2 + \Gamma^2}, \qquad (8)$$

$$\Gamma = \text{Im}\,\Sigma(\omega) = \pi\rho(\omega)\,V^2. \qquad (9)$$

Here $\rho(\omega)$ is the density of states in the conduction band. Thus we have obtained a virtual f level of width Γ whose position is determined in self-consistent fashion in terms of the occupation numbers of the f and s levels n_f and n_s by the equation[6]

$$n_f = \int_{-\infty}^{E_F(n_f)} \rho(\omega)\,d\omega = \frac{1}{\pi} \text{arcctg}\, \frac{E_0 + Gn_s - E_F(n_f)}{\Gamma} \qquad (10)$$

(for a constant density of states ρ, and correspondingly, constant Γ).

Equation (10) is a generalization of the self-consistency equation in the Falicov model including hybridization. In form it resembles the corresponding equation in the Anderson model. Using the fact that $E_F(n_f) = E_F(1) + (n_s/\rho) - Gn_s$ and that $n_f + n_s = 1$, we can easily

analyze Eq. (10) and find that the number of f electrons varies with increasing E_0 either jumpwise or smoothly, depending on the ratio of the parameters V (i.e., Γ) and G; see Fig. 11. Thus, as qualitative considerations also imply, $f-s$ hybridization makes the EPT more diffuse. Near the transition we now have $n_f \neq 0$ or 1. That is, an intermediate valency appears.

Taking into account the periodicity in the arrangement of the centers would have the result in the spin-free model that the spectrum would show a hybridized gap instead of a virtual level (a peak in the density of states of width Γ; see Fig. 5). The fundamental qualitative conclusions about the character of the transition are not altered.[90] In the complete model of Eq. (5), owing to the strong correlations of the f electrons at a center, the gap in the spectrum is apparently in any case blurred out,[90,91] while the characteristics of the EPT can become more complicated.[99]

For systems of the SmS type, where the f level emerges from the gap into the conduction band (see Fig. 2, a–c) and where the EPT is simultaneously a dielectric-metal transition, we must include the fact that the density of states is $\rho(\varepsilon) = 0$ for $\varepsilon < 0$, and $\rho(\varepsilon) \approx \sqrt{\varepsilon}$ for $\varepsilon > 0$. As Eq. (4) and Fig. 10c imply, in this case, even in the absence of hybridization, the number of f electrons before the transition can be $n_f < 1$. In the presence of hybridization we must include in (6)–(9) the level shift due to $\text{Re}\Sigma(\omega)$. Here, even while the renormalized level lies below the bottom of the conduction band, the fraction of f electrons in it is already less than unity.[92,93]

$$n_f = \int_{-\infty}^{\mu} \delta(\omega - E_0 - \Sigma(\omega))\,d\omega = \left(1 - \frac{d\,\text{Re}\,\Sigma}{d\omega}\Big|_{\omega = \tilde{E}_0}\right)^{-1}. \qquad (11)$$

Here μ is the chemical potential, and $\tilde{E}_0$ is the renormalized energy of the f level, given by solving the equation

$$\tilde{E}_0 - E_0 - \text{Re}\,\Sigma(\tilde{E}_0) = 0. \qquad (12)$$

The complete model of (5) including spins has been treated in the SCF approximation both for $f-s$ and for $f-f$ interactions[83]; here first-order transitions proved possible from the nonmagnetic state with small $n_{f\uparrow} = n_{f\downarrow}$ to the magnetic state with $n_{f\uparrow} \neq n_{f\downarrow}$, $n_f \approx 1$. Analogous results have been obtained by Haldane,[89,94] who reduced the $f-s$ interaction to the interaction of an f electron with a boson field describing the density fluctuations of the s electrons. In Ref. 82, the $f-f$ interaction in the model of (7) was taken into account in the
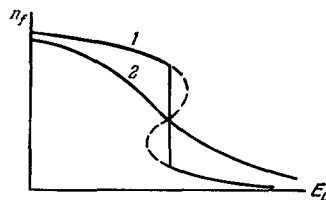

FIG. 11. Dependence of the occupation of the f level in the Falicov model on E_0 including hybridization of the f electrons with the conduction electrons. 1—weak hybridization, $\pi\Gamma < 2G - (1/\rho)$; 2—strong hybridization, $\pi\Gamma > 2G - (1/\rho)$.

Hubbard approximation.[95] This does not alter the conclusions qualitatively, leading only to a certain asymmetry in the $n(E_0)$ dependence.

One can also treat the EPT including effects of hybridization at finite temperatures.[84] The corresponding results are close to those given above for the original Falicov model.

3) *Going outside the framework of the self-consistent-field approximation and including exciton correlations.* As we see from the last section, including $f-s$ interaction in the SCF approximation gives rise to first-order transitions directly between states of integral valency. However, apparently the tendency to a jump is somewhat exaggerated here. Actually, when we depart from the framework of the SCF approximation, even the $f-s$ interaction itself contains factors that smooth out the transition and stabilize an IVS. Physically they involve the importance of including local correlations of the f and s electrons or of the s electrons and f holes, i.e., exciton effects. Actually, the strong tendency to a first-order transition has been associated with the term Gn_s^2 quadratic in n_s in (3) and (4), which arises precisely in the SCF approximation (interaction of *all* the f electrons with *all* the conduction electrons). But if we include the local correlations of a given s electron with some f hole (which are important, at least when their concentration is small), then evidently the accelerating effect of this term will be weakened, and a fixation of the f level near the Fermi level becomes more probable.

The first realization of this idea was carried out in Refs. 96 and 97. They used the generalized Hartree-Fock approximation, which includes exciton correlations and resembles the approximation employed in treating excitonic insulators.[98] Specifically, a very general decoupling was performed in the term for the $f-s$ interaction of the form

$$\frac{G}{N} \sum_{k,k',m} a_k^+ a_{k'} \cdot c_m^+ c_m \rightarrow Gn_s \sum_m c_m^+ c_m + Gn_f \sum_{k,k'} a_k^+ a_{k'}$$
$$+ \frac{1}{\sqrt{N}} \sum_{k,m} (\Delta a_k^+ c_m + \text{h.c.}),$$
$$\Delta = \frac{G}{V\sqrt{N}} \sum_k \langle a_k c^+ \rangle. \tag{13}$$

The anomalous mean Δ describes the electron-hole correlation and is determined self-consistently. As we can easily see, this decoupling reduces the problem to that treated in Sec. 2, but with the substitution $V \rightarrow \tilde{V} = V + \Delta$.

As analysis shows, including exciton correlation of this type actually smears out the transition. In particular, in the periodic model of Falicov the transition in this approximation is smooth for any values of G.[70] Apparently the situation is the same also in the "impurity" variant.[173] [In Refs. 96 and 97, the quantity Γ was found in the weak-coupling approximation; here the jumpwise transition (or two successive transitions) can be maintained if there is another additional mechanism of attraction of the electrons that increases the term $-Gn_s^2$ in the energy of (3). For example, such a

mechanism could be electron-lattice interaction.[173] But in the "pure" model of Falicov the transition is continuous.]

The suppression of a discontinuous transition in this approach is related to the fact that, as is evident from (10), a first-order transition arises under the condition $2G - (1/\rho) > \pi\Gamma$, while the quantity $\Gamma = \pi\rho V^2$ increases strongly with increasing G in the decoupling of (13). Perhaps inclusion of exciton correlation by using the uncoupling of (13) smooths the transition excessively, though qualitatively the corresponding tendency is undoubtedly precisely of this type.

We note that it is extremely hard to justify the approximation (13) for narrow f levels. One can show[161] that the spin-free model of Falicov with hybridization [see (5)] is exactly equivalent for an isolated impurity to the Kondo model

$$\mathcal{H}_K = \frac{1}{2} J_\perp (s^+ \sigma^- + \text{h.c.}) + J_\| s^z \sigma^z. \tag{14}$$

Here we have $J_\perp \sim V$, while $J_\| \sim f(G)$. When $V = 0$ [or, in (14), $J_\perp = 0$], this model can be solved exactly.[101] However, as we know, it shows an essential singularity as $V \rightarrow 0$ (see also Ref. 94). The approximation (13)[96,97] recalls the approximation of Nagaoka in the Kondo problem.[102] As we know, although the latter does not reflect many subtle features of this phenomenon, it qualitatively describes the situation quite reasonably (for values of $J_\perp$ that are small but nonzero). We may hope that the situation is the same in this case. Interestingly, the approximate treatment of the Falicov model without hybridization employing decoupling of the equations of motion,[103] which also takes account of exciton effects and is exact for the case of a single impurity,[101] yields results that are very close to those discussed above (the difference involves mainly the choice in Ref. 103 of an asymmetric density of states of the form $\rho(\varepsilon) \sim \sqrt{\varepsilon}$ at the edge of the band). As Schweitzer states,[103] the jumpwise nature of the transition is maintained here.

A number of studies have employed the approximation of a coherent potential in discussing Falicov's model (without hybridization). Here they considered the rare-earth ions of differing valency to be the (statistical) components of a binary alloy. This method also allows one to include local correlations of s electrons and f holes. The results of these studies are contradictory: Refs. 121 and 152 obtained a first-order transition in a certain region of values of the parameters, while it is always smooth according to the statements of Refs. 169 and 170.

Yet another approach to treatment of exciton effects in IVSs has been proposed by Kaplan, Mahanti, and Barma.[105,106,106] They started by treating the conduction electrons (d electrons) as being to a certain extent localized. There are now some experimental grounds for such a treatment.[69,107,7)] The factor responsible for

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7)Actually, this is not a two-band, but a three-band model (narrow d and f levels and a broad conduction band in which, as estimated in Ref. 106, there are about 0.1 electrons per center). This model can explain a number of experimentally

the mixing of the $4f$ and $5d$ states and for the consequent nonzero mean $\langle ac^{+}\rangle$ in Kaplan's model was considered to be not the matrix elements for hybridization nor the direct Coulombic interaction of the f and $s(d)$ electrons, but the term in the Hamiltonian of the form $\xi_{ij}c_i^{+}c_j^{+}a_j a_i +\text{h.c.}$, which describes the simultaneous excitation of two neighboring centers, and also the analogous term of the form $\xi_{ij}c_i^{+}a_j^{+}a_i c_j$. Actually the quantity ξ_{ij} is the matrix element for van der Waals interaction. One of the consequences of Kaplan's model is the existence in an IV phase of a dipole moment at a center, with possible ordering at low temperatures. The transition itself is smoothed out owing to the included terms, both because of direct hybridization or the exciton effects treated above.

4) *General treatment of the electronic system.* Thus far we have been basing our treatment on the simple model of Falicov, which included only the (short-range) direct interaction of the f and s electrons, while neglecting the long-range forces and, say, the exchange terms in the energy. Even in this simple model it proved possible to describe the phase transition itself, to include local (exciton) correlations, and to obtain an IVS. However, in order to describe more subtle effects, such as the character of the transition itself and the detailed type of the ground state, etc., the approximations made in formulating the model and solving it may prove insufficient.

A somewhat different, rather general approach to treating these problems can be based on the study of the total energy of the electronic system, just as is done in studying the electron gas in metals[109,110] or the electron-hole fluid in semiconductors.[111,112] In this approach the energy of the system has the following form[113]: [cf. (4)]

$$\mathscr{E} = E_g n - E_{\text{exch}} n^{4/3} + E_{\text{kin}} n^{5/3} - E_{\text{inter}} n^{2}. \tag{15}$$

Here $n = n_s$ is the concentration of conduction electrons, the second term is the exchange energy, the third term is the kinetic energy of the electrons, and the last term is their interaction. The signs in (15) are chosen so that all the constants E_i are positive. An important point is that Eq. (15) holds also in an excitonic, i.e., dielectric phase.[8,113]

We can directly draw the following conclusions from Eq. (15), even without a detailed calculation of the coefficients E_i:

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observed properties of SmS. Yet apparently it contradicts the above-noted circumstance that the concentration of conduction electrons in the metallic phase of SmS, as directly measured,[3] is ~1 per atom. Apparently the strict separation of the d electrons into localized ones (~90%) and free ones (~10%) that is made in Refs. 105 and 106 is somewhat arbitrary, and all these electrons possess some intermediate character.

[8] In such a phase the last term in (15) has the meaning of the exciton-exciton interaction. Exciton correlations, which were discussed in the last section, cause this interaction to be numerically substantially smaller than the analogous interaction in (3). This is essentially precisely why exciton effects smooth out the transition.

a) At low temperatures an EPT from a state with $n = 0$ that occurs with decrease of E_g (e.g., under the action of external pressure) must in principle be a first-order transition [the function $\mathscr{E}(n)$ of (15) has a negative curvature for $n \to 0$].

b) Depending on the relationship between the constants E_i entering into (15), we can have either: 1) a direct transition from a phase with $n = 0$ to a phase with $n = 1$; or 2) a first-order transition from $n = 0$ to an IVS with $0 < n < 1$ and then another jumpwise transition to a phase with $n = 1$; or 3) a first-order transition from $n = 0$ to an IVS and then a smooth increase in n without jumps. It is rather hard to find the exact form of the individual coefficients entering into (15) (see Ref. 114), especially in the limit of small concentration. An especial complication can arise from taking account of the "heavy" f component, which apparently forms some type of Fermi fluid at low temperatures.[16,164] However, in principle this approach seems highly promising, not only for studying the character of an EPT, but also for studying the nature of the ground state, for elucidating the possibility of "crystallization" of the heavy f holes, etc.

5) *Electron-lattice interaction.* Another factor besides electron-electron interaction that has been adduced for explaining the characteristics of EPTs in rare-earth compounds is electron-lattice interaction.[93,97,113,116,117] Physically its importance involves the abovementioned fact that the ions of different valency between which the transition occurs have strongly differing ionic radii (by 15–20%). Correspondingly, the EPT is usually accompanied by an appreciable change in the lattice constant (e.g., in the system $Sm_{1-x}Gd_xS$ the transition can generally be explosive in nature and destroy the specimen[36]). This same situation also is related to the fact that those transitions are rather easily induced by external pressure.

In treating electron-lattice interaction, it is expedient to distinguish interaction with the homogeneous deformation and with phonons at a given deformation. We shall first give a very simple phenomenological scheme[97] that shows that in the self-consistent field approximation including the interaction of the electrons with a homogeneous deformation leads qualitatively to the same conclusions for the EPT as $f - s$ interaction does.

The relative position of the f level and the conduction band as characterized by E_0 actually depends on the atomic volume v. Let us take account of this relationship in the linear approximation

$$E_0(v) = E_0(v_0) - a(v - v_0), \quad a > 0. \tag{16}$$

Here a is a phenomenological parameter. We can easily write an expression for the energy of the system including the $E_0(v)$ relationship and with inclusion of the lattice energy [cf. (3)]

$$\mathscr{E} = \mathscr{E}_{\text{el}} + \mathscr{E}_{\text{lat}} = [G - E_0(v)]n_s + \frac{1}{2\rho}n_s^2 - Gn_s^2 + \frac{B_0}{2v_0}(v - v_0)^2, \tag{17}$$

B_0 is the original bulk modulus. Upon varying the energy [or more exactly, the enthalpy $\mathcal{K} = \mathscr{E}$

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+$P(v - v_0)$, where P is the external pressure] with respect to v, we get

$$\frac{v-v_0}{v_v} = -\frac{P+an_s}{B_0}. \tag{18}$$

Then, upon substituting (18) into (17), we find

$$\mathscr{H}(n_s) = -\left[E_0(v_0) + \frac{av_0}{B_0}P - G\right]n_s + \frac{1}{2\rho}n_s^2 - \left(G + \frac{a^2v_0}{2B_0}\right)n_s^2 + \text{const.} \tag{19}$$

Hence we see, first, that the effective position of the f level is shifted linearly upward with pressure, and second, that including the interaction with the deformation leads to the appearance in the energy of a term $-(a^2v_0/2B_0)n_s^2$, which is exactly analogous in its structure and action to the term $-Gn_s^2$ in (3). Correspondingly, all the conclusions about the character of a phase transition under pressure that were discussed in Sec. 2 remain in force in this model.

Qualitatively it is easy to understand the tendency toward jumpwise transition owing to electron-lattice interaction. Suppose the f level initially lies below the bottom of the conduction band (or the Fermi level) and let a certain number of f electrons be excited from it into the s band. Correspondingly, n_s ions of higher valency will arise in the system and will have a smaller radius. In the SCF approximation this is equivalent to a decrease in mean lattice parameter or in the atomic volume v. In line with (16), this increases the energy E_0 of the f level, i.e., decreases the activation energy needed for further transition of electrons from the f level to the conduction band. Under certain conditions this "feedback" becomes sufficient to cause an avalanche-like process with transition of all the f electrons to the s band and with a corresponding decrease in the lattice parameter.

Thus, just as in Falicov's model, one can't obtain states with an IV after the transition directly in this treatment. One of the factors that have been adduced in this model for explaining the stabilization of an IVS is to include the nonlinear compressibility.[93,116,117] It is known empirically that the lattice compressibility usually declines with decreasing atomic volume. Varma and Heine[93] have taken account of this factor phenomenologically by the choice

$$B_0(v') = B_0(v)\left(\frac{v}{v'}\right)^\gamma, \quad \gamma \approx 1.3. \tag{20}$$

Hirst[116] considered this same mechanism using the Birch equation, according to which the elastic energy of the deformed lattice is written in the form

$$\mathscr{E}_{\text{lat}}(v) = \frac{9}{8}B_0v_0\left[\left(\frac{v_0}{v}\right)^{4/3} - 2\left(\frac{v_0}{v}\right)^{2/3} + 1\right]. \tag{21}$$

Both approaches are physically equivalent and yield similar results: one can choose the phenomenological parameters in such a way that, as the transition progresses, the compressibility of the system declines so much during its compression that the transition is hindered and is stopped before completion at some intermediate value $n_s < 1$. This corresponds to formation of an IV phase after the transition.

There is another physical mechanism that can substantially alter the pattern and stabilize an IVS. We can convince ourselves that this happens if the strongest

interaction is that of the electrons with short-wavelength optical phonons, rather than with the homogeneous deformation. We shall illustrate this with a model with local d electrons. We can write a Hamiltonian of the electron-phonon interaction that takes account of the relative change in the energy of the f and d electrons with change in atomic volume in the following form, after transformation to phonon operators (we assume that $n_{fi} + n_{di} = 1$ owing to electroneutrality):

$$H = \varepsilon_0\sum_k a_k^+a_k + E_0\sum_m c_m^+c_m + \sum_{q,\,\alpha}\omega_{q\alpha}b_{q\alpha}^+b_{q\alpha} + \sum_{m,\,q,\,\alpha}g_{mq\alpha}c_m^+c_m(b_{q\alpha}^+ + b_{-q\alpha}). \tag{22}$$

Here the $b_{q\alpha}$ are the operators for a phonon of mode α with the momentum q.

Direct application of the SCF approximation with respect to the electrons and phonons to the Hamiltonian of (22) (i.e., replacement of $c_m^+c_m$ and $b_{q\alpha}^+$, $b_{q\alpha}$ for $q=0$ by c-numbers) leads to an energy in the form of (19).

However, in this approximation we have not included local effects, or in other words, we have not separated out the self-action. An approach that includes these factors consists in eliminating the electron-phonon interaction [the last term in (22)] by using a shift transformation (see, e.g., Ref. 100):

$$b_{q\alpha} \to \gamma_{q\alpha} = b_{q\alpha} + \sum_m\frac{g_{mq\alpha}}{\omega_{q\alpha}}c_m^+c_m \tag{23}$$

or the equivalent canonical transformation

$$H \to \tilde{H} = e^{iR}He^{-iR}, \quad R = i\sum_{m,\,q,\,\alpha}\frac{g_{mq\alpha}}{\omega_{q\alpha}}c_m^+c_m(b_{q\alpha}^+ - b_{-q\alpha}). \tag{24}$$

Hence we find

$$\tilde{H} = \varepsilon_0\sum_k a_k^+a_k + \sum_m\left(E_0 - \sum_{q\alpha}\frac{|g_{mq\alpha}|^2}{\omega_{q\alpha}}\right)c_m^+c_m + \sum_{q\alpha}\omega_{q\alpha}\gamma_{q\alpha}^+\gamma_{q\alpha} + \sum_{m\neq m'}J_{mm'}c_m^+c_mc_{m'}^+c_{m'}, \tag{25}$$

$$J_{mm'} = -\sum_{q\alpha}\frac{g_{mq\alpha}g_{m'q\alpha}^*}{\omega_{q\alpha}} = -\sum_{q\alpha}\frac{|g_{q\alpha}|^2}{\omega_{q\alpha}}e^{iq(m-m')}. \tag{26}$$

We see from (25) and (26) that, first, the self-action term has been separated out (constant shift of the f level—actually a polaron shift), and second, an interaction of f electrons at different centers has appeared. This is precisely what yields terms quadratic in n in the energy. The magnitude and sign of this interaction depend essentially on the dispersion of the phonons and on the matrix element for electron-phonon interaction. Its corresponding contribution to the quadratic terms of the energy is considerably smaller than in the SCF approximation and can even differ in sign. Actually, for example, in SmS, besides the interaction with the homogeneous deformation [which also reduces to the form (25) with $J_{mm}^{\text{def}} = \text{const} < 0$], a very substantial interaction is that of the f electrons with the totally symmetric vibrations of the anions near the Sm ion ("breathing-type mode"), i.e., mainly with the longitudinal optical vibrations at the L-point on the face of the Brillouin zone.[124] Consequently the total interaction of the f electrons via these phonons is repulsive

in nature.[9] It does not sharpen, but on the contrary, smooths out the EPT and stabilizes the phase in an IV. We can easily see from the standpoint of this interaction that the most favorable configuration would correspond to spatial ordering of the rare-earth ions having differing valencies[10] (this might be called a valence-density wave[119]). Qualitatively this is quite natural: upon interaction with phonons having $q \approx \pi/d$, the compression of the shell of the sphere around a given Sm ion [which stabilizes the (sd) state in it] corresponds to a stretch near the adjacent centers (f state).

Actually, spatial ordering in an IVS has not yet been observed (perhaps an indication of such an ordering is the periodic modulation of the magnitude of the magnetic moment found in CeAl$_2$[67]); most likely, even if such spatial correlations exist in these systems, they must have the character of short-range order of the type existing in a liquid. The $f - s$ transitions caused by hybridization and the free movement of the electrons in the s band will "break down" this ordering. A simultaneous inclusion of these terms in the electron-phonon interaction is rather complicated, even within the scope of the simplest models. This is related mainly to the noncommutation of the operators $c_m^{+} c_m$ that enter into (24) and of $a_k^{+} c_m$ in the hybridization term. Consequently, in particular, a decline in effective hybridization can occur, $V \to \tilde{V} \approx V \exp(-g^2/\omega^2)$[118] (analogous to polaron band narrowing). In turn, the rather large value of the hybridization and the width of the s band can suppress polaron effects,[59] and apparently bring the situation closer to that described by the SCF approximation. Apparently the true situation is something intermediate. An attempt to model it has been made[104,119] by the variational method. The wave function of a center was sought in the form $|\psi_m\rangle = u a_{ml}^{+} |0\rangle \| \beta_a \rangle\rangle + v c_m^{+} |0\rangle \| \beta_f \rangle\rangle$. That is, the different electronic components each entered with its own deformation $\| \beta_i \rangle\rangle(b^{+}\| \beta_i \rangle\rangle = \beta_i \| \beta_i \rangle\rangle)$. The parameters u, v, β_a, and β_f were sought from the condition of minimum energy. Owing to the "hybrid" character of the approximation, the results proved intermediate between the conclusions of the SCF approximation and the case of limiting polaron

correlations. It actually turned out that including local effects smooths out the transition. The degree to which they are manifested (in particular, the degree of suppression of hybridization) depends not only on the relationship of the constants V, g, and ω, but also on the position of the f level with respect to the conduction band.

6) *Phase diagrams.* Figures 3 and 7 show examples of phase diagrams in an EPT with valency change. A number of problems arise in discussing the factors that govern the nature of the phase transition and the form of the phase diagrams.

The first problem concerns the nature of the transition. As a rule, EPTs are isomorphous and are not accompanied by a change of lattice symmetry. In this case the transition can be either continuous (diffuse) or a first-order transition. The general arguments of Sec. b, 4 imply that apparently the transition must be first order at low enough temperatures. This is precisely the situation in Ce and SmS. It is currently not clear whether this is always true. From this standpoint it would be highly desirable to study the EPT at low temperatures in SmSe and SmTe, in which the transition is continuous at room temperature.

The second problem is whether the transitions with valency change are "single" or "double". Usually one observes transitions from a state of integral (or almost integral) valency (the f level lies below the Fermi level) to an IVS ($E_0 \approx E_F$). Upon further change in the parameters, e.g., a pressure increase, in principle a second transition can occur from the IVS again to a phase with integral valency where $E_0 > E_F$. This is the situation in Ce (the change of lattice symmetry in the $\alpha - \alpha'$ transition can be a secondary effect), and also apparently in SmS.[40] Existence of three different phases has also been found in TmTe.[49,11] It is not fully clear at present whether this situation is general, nor in which cases the second transition will be first-order and when it will be smooth. (From this standpoint, it would be very interesting to study the properties of SmS in the 20-kbar region at low temperatures).

The problem of the asymmetry of the transition is closely connected with this problem: as a rule, if the transition is single, an IVS is realized *after* the transition. However, very simple theoretical treatments usually yield a transition symmetric with respect to $n = 1/2$, and sometimes even lead to the inverse situation (see Figs. 9b and 10c). The possible reasons for the observed asymmetry are discussed in the next section.

And finally, an important problem is to elucidate the factors that determine the character of the transition upon change of temperature, in particular, the slope of the phase equilibrium line. Here we can propose the

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[9]Anderson and Chui[113] have presented arguments that, when one includes anharmonic effects, the interaction with a homogeneous deformation can also lead to repulsion of the f electrons, rather than attraction.

[10]This becomes especially graphic if we use the pseudospin formalism. Upon introducing the pseudospin operators $\sigma = 1/2(c_m^{+} c_m \to (1/2) - \sigma_m^z, \ a_m^{+} a_m \to (1/2) + \sigma_m^z, \ a_m^{+} c_m \to \sigma_m^{+}, \ c_m^{+} a_m \to \sigma_m^{-})$ to describe the state of a center, we can write the effective Hamiltonian of (25) in the form $\sum_{m \neq m'} J_{mn} \sigma_m^z \sigma_n^z - h \sum \sigma_m^z$, $h = \tilde{E}_0 - \varepsilon_0$. Hence, evidently, in the "ferromagnetic" case [$J(q)$ maximal for $q = 0$, attraction of f electrons], the transition with change of h (increasing E_0) will be a jumpwise transition between states of integral valency (at $T = 0$), $nf = 1 \to 0$. Yet in the case of repulsion of the f electrons [the "antiferromagnetic" case, $J(q)$ maximal for $q = \pi/d$], the state is "ferromagnetic" ($\sigma^z = -1/2$, i.e., $n_f = 1$) when $h < h_c \approx J_{max}$ (deep f level), but "antiferromagnetic" for $-h_c < h < h_c$ (centers alternate having $n_f = 0$ and $n_f = 1$; an IVS!), and $n_f = 0$ when $h > h_c$. Thus two successive transitions occur here with increasing E_0 with a spatially ordered IV phase between them.

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[11]An isomorphous first-order transition at 26 kbar from an IV phase has recently been found in Sm$_4$Bi$_3$.[115] It is not yet clear whether it is a transition to a phase with Sm^{3+} or to another IV phase.

following ideas (see also Refs. 5, 108, and 123).

At low enough temperatures in IV phases, the electrons apparently form a Fermi fluid with a "heavy" mass, a low degeneracy temperature $(T_F \approx \Gamma)$, and high density of states at the Fermi surface. Its entropy is determined by the well known expression[122] $S_{F.f.}$ $= (\pi^2/3)N(0)T$. The lattice entropy at low temperatures varies as $\sim T^3$ and its contribution is not substantial. Consequently we can expect that a transition will occur with increasing temperature to a phase with higher density of states $N(0)$. Such a phase is an IV phase. Hence a transition must occur with rising temperature from a phase of integral valency $(n_f \approx 0, n_f \approx 1)$ to an IV phase. Of course, this argument is valid if one of the bounding phases contains no other ordering (magnetic, superconductive).

The spin and lattice entropies come into play with further temperature increase. At the same time, when $T \gtrsim \Gamma$, the electronic entropy no longer plays a substantial role. The spin entropy has the effect that the high-temperature phase proves to be the one having (disordered) localized magnetic moments.[81] The lattice contribution tends to cause a transition to a phase having phonons of lower frequency. Usually this is a phase of large specific volume [see (20) and (21)]. That is, a lattice mechanism of transition yields $dT_c/dP > 0$. However, the phonons can be further softened in an IV phase. In such a case this state would be stabilized with increasing temperature. In a number of cases, we must also take account of the entropy involving the detailed multiplet structure of the terms of the corresponding ions.[123] It is important if the electrons are localized in character. This contribution to the entropy is not as universal as that treated above, but in certain concrete cases it can be very important.

An additional factor that affects the form of the phase diagram and is specific for IV phases can also be exciton correlations, which decrease the entropy of this phase.[96-98] This mechanism would stabilize the IVS at low temperatures.

As a whole, the situation concerning the thermodynamics of EPTs and the phase diagrams is still indefinite. Additional experiments are needed for elucidating the relative role of the different factors in determining the character of the phase transitions and the form of the phase diagram in various concrete systems.

7) *Electronic phase transitions and stabilization of intermediate-valency phases.* Thus, in summarizing this chapter, we must say that the theories that have been developed, which describe in general outline the features of EPTs in the compounds, studied nevertheless cannot answer a number of questions at the present time. The relative role of the different physical mechanisms in the transition is unclear, and the problem of the form of the phase diagram is not fully clear. We do not know whether in principle such transitions can be second-order transitions or whether they are always first-order at low enough temperatures, while continuous transitions correspond to

supercritical conditions. However, the fundamental problem is why an IV phase always arises in these transitions, usually following the transition. Let us list again some mechanisms that have been adduced to explain this.

A. The f level is fixed to E_F if the kinetic energy needed to displace electrons in the conduction band is larger than the energy gain here. A variable density of states (e.g., $\rho(\varepsilon) \sim \sqrt{\varepsilon}$) leads to asymmetry of the transition.

B. The IV phase can be stabilized by increase of the width of the level $\Gamma = \pi \rho V^2$. Section b, 3 has discussed this mechanism of appearance of an IVS with exciton broadening of the level. However, Γ can be increased simply by an increase of the matrix element for hybridization. Actually, hybridization is due to overlap of the f orbitals at a center with the d orbitals of *adjacent* centers,[5] and it must increase with compression. A direct experimental indication of the importance of this mechanism might be the increase in the characteristic energy of the spin fluctuations from 20 MeV to >70 MeV in the $\gamma - \alpha$ transition in $Ce_{0.74}Th_{0.26}$.[69]

C. A third factor that stabilizes an IVS is the decreased compressibility in a transition that leaves the EPT "halfway". Apparently this factor is rather general.

D. Finally, local effects (excitonic, polaronic) facilitate formation of an IV. They do not lead *per se* to asymmetry of the transition; apparently their role consists primarily in weakening the tendency to jumpwise transition.

It is as yet hard to say which of the factors listed is most important. Perhaps some of them act jointly. On the whole, there is still no final answer to the question of the reasons for stabilization of IVSs. Essentially, this problem is closely connected with the problem of what constitutes an IV state itself, and we can hope to get a real answer to it only along with understanding of the structure and properties of this state.

4. INTERMEDIATE-VALENCY STATES

a) An overall picture of intermediate-valency states

Let us proceed to treat the very interesting set of problems of the properties of the IV state itself. We should say that a qualitative picture of IV phenomena has already crystallized out, at least at a level satisfying the first inquiries of the experimentalists. However, essentially we are still far from a complete understanding of the corresponding phenomena. One of the aims of this chapter is, in particular, to formulate the unsolved problems as clearly as possible.

Before proceeding to discuss the experimental properties of IV compounds, let us examine how in principle such a state might be "organized". Various situations are possible here.

First of all, the ions of different valency can exist statistically and occupy nonequivalent positions in the

crystal structure. For example, this is the situation in Eu_3O_4. This case is not very interesting.

Also, a situation is possible in which the ions of different valency occupy equivalent positions, but electron exchange between them proves relatively slow and involves thermally activated hopping. This case has been termed an inhomogeneous IV. Objects of this type are also known: they include the compounds Eu_3S_4, Sm_3S_4, and a number of others. Actually, a number of well-known compounds of the transition metals belong to this class, e.g., magnetite Fe_3O_4.[125] Apparently the so-called Magneli phases of the oxides of Ti and V have analogous properties.[125] At high temperatures the exchange between the ions of different valency occurs rather rapidly (the characteristic time for hopping depends exponentially on the temperature, $\tau \approx \tau_0 e^{-\Delta E/kT}$). This is manifested in the considerable conductivity of these compounds at high temperatures. The characteristic times increase sharply with decreasing temperature, and the situation becomes close to static. Here spatial differentiation and ordering of the ions of different valency can occur (a phenomenon analogous to Wigner crystallization[126]). It is usually accompanied by decrease of lattice symmetry. This phenomenon has been found in magnetite and in mixed oxides of Ti and V.[125,127] The same behavior has been established also in Eu_3S_4,[21,25,128] in which the hopping time increases from 10^{-11}s at room temperature to $>10^{-7}$s at $T \approx 150$ K. Apparently charge ordering occurs in this system at 160 K. There are indications of similar behavior in Sm_3S_4.[20,21]

And finally, the most interesting case is that of a homogeneous IV, to which most of the compounds thus far mentioned belong.[12] They are characterized on the qualitative level by rapid transitions between the states of different valency at each center. These transitions have a quantum nature, and arise from the nondiagonal matrix elements of the Hamiltonian of the type of the hybridization terms $V_{km}a_k^+c_m$, and also perhaps from the analogous terms in the Coulombic (and electron-phonon) interaction. Consequently the f level for an isolated center acquires a finite width Γ; see (9) (the characteristic time of the transition is $\tau_{ICF} = \hbar/\Gamma$). At high enough temperatures, the corresponding charge fluctuations at different centers prove to be incoherent. For example, in this case they can contribute to the resistance. However, as $T \to 0$, some coherent state must be established. What its character is and at what temperature this coherence arises is a cardinal problem of the entire physics of IV materials.

As we have seen in the last chapter, IV states generally arise in an EPT with change of valency. We can view them as resulting from a phase transition that hasn't been completed and is extended over a finite region of pressure, temperature, etc. From this standpoint an IV phase is, so to speak, a state "inside"

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[12] When not expressly stipulated, the term "intermediate valency" is employed in this review precisely for compounds of this class.

the phase-transition region. This approach allows one naturally to understand an entire set of features of this phase as "extended" features of the phase transition. Though this picture is not rigorous, it gives a correct general orientation and in some cases can even suggest what specific phenomena can be observed in an IV phase.

b) Properties of intermediate-valency compounds and their interpretation

The behavior of almost all characteristics of the substance are anomalous in an IV phase. We shall begin by discussing the lattice properties.

1) *Lattice properties.* Since lattice effects play a substantial role in transitions involving change of valency, naturally, many lattice characteristics exhibit peculiarities that involve these transitions and the onset of an IVS. Besides the intermediate value of the lattice parameter itself, the behavior of the thermal expansion coefficient often proves anomalous. Thus, for example, in $Sm_{1-x}Gd_xS$ with $x \approx 0.0.25-0.30$ in the metallic phase, which is an IV phase, the interatomic distance increases either upon rise or fall of temperature (in approaching the transition boundary $M-B'$; see Fig. 7). Analogous anomalies in thermal expansion have also been observed in some other substances.

The elastic properties and phonon characteristics of IV substances possess a number of peculiarities. As a rule, the compressibility proves anomalously large in an IV phase.[117,129] We can easily understand this from the arguments developed in Chap. 3, Sec. b, 5. In an IV phase, besides the ordinary compressibility for a substance with fixed ion cores, the volume of the system is diminished in addition by transition of a fraction of the f electrons to the conduction band and by the corresponding decline in the ionic radii. We see from Eq. (18) that the compressibility of the system is

$$\varkappa = -\frac{1}{v}\frac{dv}{dP} = \varkappa_0\left(1 + a\frac{dn_s}{dP}\right). \tag{27}$$

Here $\kappa_0 = 1/B_0$ is the compressibility of the substance in the normal phase. Actually the large compressibility of an IVS is closely connected with the large density of states at the Fermi level $N(0) \sim 1/\Gamma$.

The increased compressibility in an IV phase can be qualitatively interpreted also on the basis of the above-noted analogy of the properties of an IVS to the behavior of a substance "inside" a phase transition. In a phase transition of the type described the compressibility increases anomalously in the region of critical fluctuations. Correspondingly, the large compressibility in an IV phase is a direct consequence of the spread of the phase transition over a finite region of variation of the parameters.

Study of Raman scattering[124] as well as analysis of the behavior of the Debye-Waller factor[120] in SmS have shown that, along with the acoustic vibrations, the longitudinal optical phonons corresponding to uniform compression or extension of the closest environment of a given f-ion are most strongly softened in an IVS. Moreover, it has been found[172] in the IV compound $Sm_{0.75}Y_{0.25}S$ that the frequencies of the longitudinal

optical phonons are smaller than for the transverse phonons practically throughout the Brillouin zone. The same occurs in certain directions for the acoustic vibrations as well. Study of phonon spectra in IV substances is just beginning. In particular, it would be interesting to study the decay of phonons, which may be sensitive to valency fluctuations and to possible local deformations that accompany them.

Study of the lattice properties of IV compounds borders on the more general problem of the role of the f electrons in lattice dynamics. Experimentally it turns out that the elastic modulis, phonon frequencies, and melting point in the rare-earth metals are substantially lower than in the neighboring transition metals, e.g., Hf.[44] A very simple explanation of these facts can involve primarily the larger specific volume of the rare-earth metals [see (20) and (21)]. However, perhaps, the cause is deeper and involves the larger polarizability of the ions in the presence of an f shell. Apparently, even a relatively small admixture of f states, or perhaps, virtual transitions to f levels lying above the Fermi level but not far from it are also rather effective in increasing the compressibility and diminishing the mean phonon frequencies[167] (apparently this is the situation in La and in a number of IV compounds, in particular, at high pressures).

2) *Magnetic properties. Relationship to the Kondo effect.* One of the first indications of the existence in some rare-earth compounds of special states (states with a homogeneous IV) was a study of the magnetic properties of SmS.[130] If an IVS were to exist in the form of a static mixture of ions of different valency, e.g., Ce^{3+} and Ce^{4+} ions in α-Ce or Sm^{2+} and Sm^{3+} in SmS, then it would be natural to expect Curie's law for the susceptibility (the corresponding contribution would enter with a weight equal to the concentration of the magnetic ions, i.e., the Ce^{3+} or Sm^{3+} ions in the given cases). Thus a magnetic ordering of some type must arise at low temperatures.

Actually this is not the case. At high temperatures one usually observes a weak temperature dependence of the susceptibility, and its value is intermediate between those for the corresponding "pure" states. As $T \to 0$, $\chi(T)$ reaches a constant value, while sometimes passing through a maximum at some intermediate temperature[11,131] (Figs. 12 and 13) (the large absolute susceptibility of Sm^{2+} involves the large Van Vleck contribution). This behavior implies the formation of a nonmagnetic state at low temperatures.

In contrast, substances with an inhomogeneous IV (Eu_3S_4, Sm_3S_4) behave normally : at low enough temperatures the Curie-Weiss law holds,[20,128] and ferromagnetic ordering is observed in Eu_3S_4 at 3.1 K.

A qualitative explanation of the nonmagnetic character of compounds having homogeneous IV, in spite of the nominal existence in them of magnetic f ions, consists in the following: the f level acquires a finite width owing to fast interconfigurational fluctuations, and if this broadening is larger than the Zeeman splitting, all the Zeeman sublevels at low temperatures are
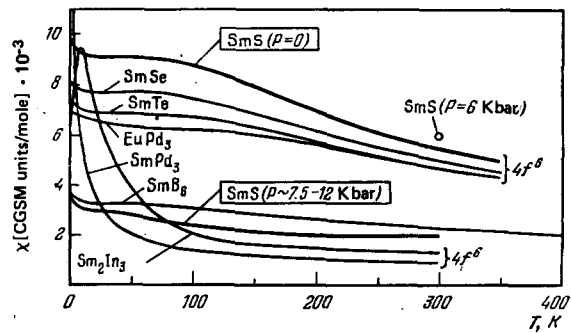

FIG. 12. Magnetic susceptibility of Sm compounds of integral and intermediate valency.[130]

occupied to the same extent, so that the susceptibility reaches a constant value as $T \to 0$. In other words, when an f electron goes from any sublevel into the s band and then returns to it, it enters with equal probability into any of the Zeeman sublevels. Thus magnetic coherence breaks down. We can qualitatively understand that the role of the Curie temperature in the Curie-Weiss law will now be played by a quantity of the order of the width Γ of the virtual level,

$$\chi(T) \sim \frac{c}{T+T_{fs}}, \qquad T_{fs} \approx \Gamma. \qquad (28)$$

Thus at temperatures $T \lesssim \Gamma$, we have $\chi(T) \approx c/\Gamma$.

We can also understand this result in another way. In an IVS the density of states at the Fermi level is $N(0) \approx 1/\Gamma$. Hence we again get the expression (28) for the susceptibility. We also see from the above that the magnetic properties of the substances discussed recall the magnetic behavior of systems showing the Kondo effect (see below).

Sales and Wohlleben[131] have given a phenomenological description of the magnetic properties of IV states based on the picture treated above. They proposed the following expression for the magnetic susceptibility:

$$\chi(T) = N \frac{\mu_n^2 \nu_n(T) + \mu_{n-1}^2 [1-\nu_n(T)]}{3k(T+T_{fs})}. \qquad (29)$$

Here $\nu_n(T)$ is the probability of occupation of the configuration $4f^n$, and μ_n and μ_{n-1} are the magnetic moments of the configurations $4f^n$ and $4f^{n-1}$. The parameters $E_{ex} = E_n - E_{n-1} \approx E_0 - E_F$ and T_{fs} are assumed
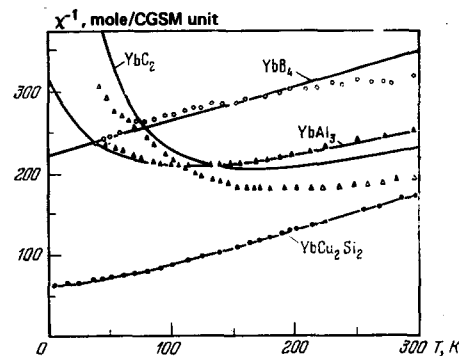

FIG. 13. Magnetic susceptibility of a set of intermediate-valency compounds.[131]

independent of the temperature and are found by best fit with experiment. Here the characteristic frequency of the fluctuations $\omega_{ICF} = T_{fs}$ is of the order of Γ (when $E_{ex} \lesssim \Gamma$). That is, Eq. (29) corresponds to the estimate of (28). According to Eq. (29), the susceptibility at high temperatures $(T \gtrsim \max(|E_{ex}|, \Gamma))$ behaves according to the Curie law, while as $T \to 0$, it reaches a constant value, while passing through a maximum at $T \approx -E_{ex}$ (when $E_{ex} > 0$, χ is maximal at $T = 0$). Figure 13 compares the results obtained by Eq. (29) with the experimental data for a series of IV compounds of ytterbium.[131]

Varma and Yafet[132] have given an approximate theoretical treatment of the magnetic properties in IV states. They strongly recall the original approach to the Kondo effect.[133] The results of Ref. 132 agree with the qualitative ideas developed above. In the case in which the f level lies in the immediate vicinity of the Fermi level, the susceptibility is given by Eq. (28) with $T_{fs} \simeq \Gamma$. But if the f level lies much deeper than the Fermi level, T_{fs} goes over into the Kondo temperature:

$$T_{fs} \approx T_K \approx E_F \exp \frac{1}{\rho J_{eff}}, \quad J_{eff} = \frac{2\Gamma}{\pi\rho}\left(\frac{1}{E_0 - E_F} - \frac{1}{E_0 - E_F + U}\right). \quad (30)$$

From this standpoint, an IV state $(E_{ex} \lesssim \Gamma)$ can be characterized as a state of a Kondo system with strong coupling and with a high value of $T_K \sim \Gamma$. The properties of such systems within the framework of Anderson's model for an isolated impurity have been treated by Haldane[134] using renormalization-group methods. He showed that that the value of the effective "Kondo temperature" for $U \gg |E_0 - E_F|$, Γ (U is the repulsion of the f electrons at a center) is given by the expression

$$T_K \approx \Gamma \exp\frac{\pi E_0^*}{2\Gamma},$$
$$E_0^* = E_0 - E_F + \frac{\Gamma}{\pi} \ln \frac{W_0}{\Gamma}. \quad (31)$$

Here $W_0 = \max\{U, W\}$, and W is the width of the conduction band. In terms of the trial parameters for $W > U$, we have

$$T_K \approx \sqrt{W\Gamma} \exp\frac{\pi(E_0 - E_F)}{2\Gamma}. \quad (32)$$

Here the susceptibility becomes $\chi \approx c/T_K$ as $T \to 0$. The expressions (31) and (32) hold for $-E_0^* > \Gamma$. The region $|E_0^*| \lesssim \Gamma$ corresponds to the IV region. In this case, as the temperature is lowered, the system goes over from a behavior corresponding to uniform occupation of the states $|f\uparrow\rangle$, $|f\downarrow\rangle$, and $|(sd)\rangle$ at $T \simeq \Gamma$ directly into a Fermi-fluid regime with an approximately constant susceptibility $\chi \sim c/\Gamma$ and with a fluctuating occupation number n_f of the f level (Fig. 14). The case of $-E_0^* > \Gamma$ is the case of the ordinary Kondo effect.[13] The results described above are also confirmed by direct numerical calculations of the susceptibility in Anderson's asymmetric model using the renormalization-group technique of Wilson.[135]

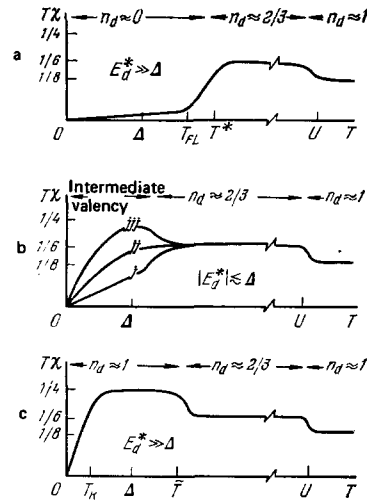Another difference of IV systems from those usually

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[13]We note that the case of the ordinary Kondo effect can also be interpreted in terms of the appearance for $T \lesssim T_K$ of a narrow resonance directly at the Fermi level.[168]

FIG. 14. Schematic behavior of the susceptibility in the Anderson model.[134] We see a transition between states of fourfold degeneracy $(T\chi = 1/8$, equally probable occupation of the states in the f level $|0\rangle$, $|\uparrow\rangle$, $|\downarrow\rangle$, and $|\uparrow\downarrow\rangle$), threefold degeneracy $(T\chi = 1/6$, occupied states $|0\rangle$, $|\uparrow\rangle$, and $|\downarrow\rangle$), twofold degeneracy $(T\chi = 1/4$, $|\uparrow\rangle$ and $|\downarrow\rangle$, localized magnetic moments present in the system) and the singlet state $(T\chi = 0$, Fermi-fluid regime). The localized level is marked by the subscript d here.

treated in the Kondo effect is the high concentration of Kondo centers (actually lying at every lattice site). In concentrated systems, the exchange interaction between the magnetic moments of the different centers can be substantial. Correspondingly, the general form of the magnetic susceptibility should most likely have not the form of (28) and (29), but an analogous form with a denominator of the type $(T + T_{fs} + T_{exch})$. In the case in which the mean value of the exchange interaction is $I \approx T_{exch} > T_{fs}$, magnetic ordering would arise in the system even before the Kondo effect and valency fluctuations had given rise to a nonmagnetic state. In the converse limiting case, as in the Kondo effect, moment compensation occurs at low temperatures, and the system is nonmagnetic. The problem of the interaction between different centers under IV conditions and of the properties of such systems is a fundamental one. Currently it is only beginning to be developed. Doniach and his associates[136,137] have studied the Kondo lattice a model of periodically arranged centers with localized spins that interact by exchange with the conduction electrons. They showed in these studies that, depending on the value of the $f - s$ exchange integral J, one can have either formation of a singlet ground state at each impurity (Kondo-type behavior) or magnetic ordering. We can understand this qualitatively by taking account of the fact that the characteristic value of the Kondo energy is $\mathscr{E}_K \simeq T_K \approx We^{-1/J\rho}$, while the characteristic energy of the exchange interaction between the impurities (the Ruderman-Kittel (RKKY) interaction with constant $I \approx \rho J^2$) is $\mathscr{E}_{exch} \approx I \approx \rho J^2 \approx J^2/W$. For small J, we have $\mathscr{E}_{exch} > \mathscr{E}_K$, and the system proves to be magnetic. Here the exchange field exerted on each spin by its neighbors suppresses the Kondo effect. Conversely, if J is large and $\mathscr{E}_K > \mathscr{E}_{exch}$, then when

$T \approx T_K$, the effective magnetic moment of the center begins to decline, so that ultimately as $T \to 0$, a singlet ground state of the Kondo type is realized at each center. This result was derived[137] by the renormalization-group method, and they found that the critical value of J is $J_c \simeq 0.4 W$. Since Doniach started directly from the Kondo model, i.e., assumed that the localized level lies rather deep beneath the Fermi surface, the IV region is not directly described in this approach. However, we can suppose that the qualitative behavior of the system (the change of regime from magnetic to Kondo-type with increasing J) corresponds to that expected even for systems with a variable position of the f level. As $E_F - E_0$ decreases, i.e., with approach to the IV region, the effective exchange interaction J_{eff} of (30) increases,[138] and we can naturally expect a transition to a nonmagnetic regime.

A similar conclusion was also reached by Varma,[139] who treated the interaction of two magnetic impurities as a function of the position of their levels with respect to the Fermi energy. He concluded that the antiferromagnetic exchange interaction of the impurities is weakened as $E_0 \to E_F$, and the system becomes nonmagnetic. However, on the whole, these results do not yet provide a full solution of the problem of many interacting centers under IV conditions, which is central to the entire physics of IV compounds.

Experimentally, the behavior of an entire set of compounds ($CeAl_3, CeAl_2$) now classifiable as IV systems very closely recalls the behavior of typical Kondo systems. There is an inverse relationship: for rare-earth impurities, the existence of a Kondo effect has been established precisely for impurities of the elements that yield intermediate-valency compounds[140] (Ce, Yb, Sm, and perhaps Tm and Eu). Most likely, this involves simply the fact that it is precisely in these systems, in which the f level lies near E_F, that exchange is appreciable. However, an even deeper connection here is not ruled out.

We have mainly been treating the case in which one of the configurations between which the transitions occur is nonmagnetic. These systems include most of the IV compounds studied up to now (see Tables I and II). The compounds of thulium in which both states of the ion, Tm^{2+} and Tm^{3+} are nominally magnetic possess a number of distinctive features. The properties of these systems were briefly discussed in Chap. 3, Sec. a, 2. They are still insufficiently understood, even qualitatively, and there are considerable contradictions in the interpretation of the experimental results. Theoretically, the behavior of these systems has not been studied at all (the first results have been announced[141]). Hence we shall not spend time on them.[14]

3) *Slow and fast measurements. Estimation of the characteristic energy of interconfigurational*

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[14]We note only a recent result in which it was found[183] that $TmSe_{0.83}Te_{0.17}$ in an IV phase has a finite magnetization in the absence of an external field.

fluctuations. As we have noted above, in IV systems characterized by the level width Γ or the fluctuation time $\tau_{ICF} \approx \hbar / \Gamma$, the results of any particular experiments depend on the relationship between the characteristic time of measurement τ_m in the given experiment and τ_{ICF} (see, e.g., Ref. 146). If τ_m is large in comparison with τ_{ICF}, then we see an averaged picture (corresponding to the mean occupation n_f of the f level). But if the experimental method is characterized by a short characteristic time $\tau_m \ll \tau_{ICF}$ ("instantaneous photography"), then the response of the system manifests the existence of states of the two types that correspond, e.g., to ions in the states $4f^n$ and $4f^{n-1} + (sd)$. One of the problems of many experiments is to determine or estimate the values of Γ and τ_{ICF}, as well as of $E_{ex} = E_0 - E_F$.

We have illustrated in the last section how one can find these quantities from static experiments with the example of analyzing the magnetic susceptibility (see Fig. 13). Another highly striking phenomenon that also allows one to estimate Γ is the anomalous behavior of the heat capacity in IV compounds. At low temperatures, IV substances show a linear electronic contribution to the heat capacity c. Here the coefficient γ in the law $c = \gamma T$ proves to be anomalously large. Whereas for typical metals the value of γ (in $mJ/\text{mole} \cdot K^2$) usually lies in the range 1–5 (in Na we find $\gamma = 1.3$, and in Ti 3.41); we have $\gamma = 12.8$ in the α-phase of Ce;[142] in the IV phase of SmS, $\gamma = 145$;[143] and in YbCuAl, $\gamma = 260$.[149] The record value of γ is that in $CeAl_3$, $\gamma = 1620$.[16]

By using the ordinary formulas of Fermi fluid theory, we can find from the heat capacity the level width Γ or the corresponding degeneracy temperature $T_F \approx \Gamma$. In typical cases, the value of Γ thus obtained proves to be of the order of 0.01–0.05 eV. The corresponding characteristic times are $\tau_{ICF} \approx 10^{-13}$ to 10^{-14} s. (In $CeAl_3$ one finds from the heat capacity $T_F = 25.3$ K.[16, 15]) One can get about the same values of Γ as from the heat capacity by starting with the values of the magnetic susceptibility at $T = 0$ (it is hard to expect agreement in the general case, since χ is altered by exchange amplification, crystal-field effects, etc.).

The determination of Γ and τ_{ICF} from the heat capacity is indirect, and it depends on the assumption that the picture of a Fermi fluid can be applied to IV systems. This problem will be discussed below, but now we shall see that information on the properties of IV systems can be gained from other experiments.

Experiments to measure the isomer shift in the Mössbauer effect are relatively "slow" (the characteristic times of measurement are $\tau_m \approx 10^{-8}$ to 10^{-10} s). In particular, this method has enabled people to see directly the variation of the characteristic time of the

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[15]Hirst[160] has started with the heat capacities for SmS and SmB$_6$ and has also obtained values of the characteristic energy of interconfigurational fluctuations of $\approx 10^{-3}$ eV. In Hirst's theory this quantity differs from the width of the virtual level in the Friedel-Anderson model $\Gamma = \pi \rho V^2$ (see also Ref. 156).

fluctuations with temperature in a compound having inhomogeneous IV, Eu_3S_4. Figure 15a shows the evolution of the Mössbauer spectra of Eu_3S_4 with temperature.[25] We see that one observes an almost static pattern (separated lines for the ions Eu^{2+} and Eu^{3+}) at low temperatures (on the time scale $\tau_m \approx 10^{-9}$ s characteristic of the Mössbauer effect in Eu_3S_4). With increasing temperature the hopping time declines strongly, so that at room temperature we have $\tau_{ICF} \ll 10^{-9}$ s, and a single line remains in the spectrum at some mean frequency. Yet in the case manifesting a single line in the spectrum down to the lowest temperatures, one concludes that this compound contains a state with homogeneous IV, with a characteristic time $\tau_{ICF} \lesssim 10^{-9}$ s (Fig. 15b).

On the other hand, the method of x-ray and ultraviolet photoemission spectroscopy[144,145] is widely applied to study IV compounds and is highly informative. In this method one studies the spectrum of the photoelectrons ejected from the material by x-ray or ultraviolet irradiation. The corresponding energies prove to be of the order of 100 eV. That is, the characteristic times of these experiments are $\tau_m \approx 10^{-16}-10^{-17}$ s. On this time scale, IV systems look like a mixture of the configurations $4f^n$ and $4f^{n-1}(sd)$ with the appropriate weights: the photoelectron spectra amount to a superposition of the spectra of these configurations, with usually well separated peaks.[23,144,145] One can find the mean valency of the compound from the relative intensities of the corresponding components.

We can conclude from the static pattern in the photoemission spectra, together with Mössbauer data, that the characteristic times of the valency fluctuations lie in the range 10^{-10} s $> \tau_{ICF} > 10^{-16}$ s. The estimate $\tau_{ICF} \approx 10^{-13}-10^{-14}$ s given above agrees with these limits. Moreover, sometimes one can directly determine the values of τ_{ICF} (or Γ) and E_{ex} by detailed analysis of photoemission experiments. Thus, the values $E_{ex} = 1550$ K and $\tau_{ICF} = 0.6 \times 10^{-14}$ s were obtained[23] for the compound $EuRh_2$.

The interpretation of the photoemission experiments requires some explanation. An IV state, at least at low temperatures, amounts to a quantum superposition of different configurations of the form $\alpha | 4f^n \rangle + \beta | 4f^{n-1}(sd) \rangle$. However, in studying photoemission, one actually does not measure directly the properties of the states $4f^n$ and $4f^{n-1}(sd)$ existing in resonance.
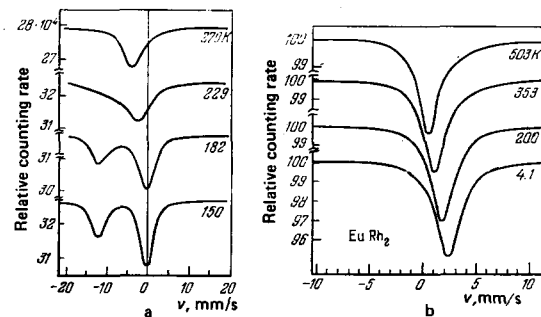
Rather, the measured spectrum characterizes the difference between the energy of the initial state, which contains n electrons, and the final state, which has one less electron. Yet the final states with $(n-1)$ electrons in different configurations now have different energies, which are generally far from resonance. Hence the photoelectron spectra for the different configurations are resolved (separated in energy).

One can also directly determine the mean valency by measuring the chemical shifts of x-ray lines,[4] as well as by studying x-ray absorption spectra.[37] Recently study has begun on IV states by neutron scattering.[69,76,147] This method allows one directly to measure the characteristic energy of the fluctuations. The values obtained also usually lie in the interval $10^{-1}-10^{-2}$ eV (indeed, in interpreting these data the problem arises of the relationship between the energies of the spin and charge fluctuations).

4. *Kinetic properties.* People usually consider IV compounds to be metals, as is implied by the absolute values of the resistivity and especially graphically by the optical properties. However, the temperature behavior of their resistivity is often not characteristic of normal metals. Figure 16 shows the temperature trend of the resistivity of the "metallic" phase of SmS.[143] Below a temperature ~100 K, one observes a considerable increase in resistivity, which imitates the trend for a semiconductor. The resistivity of SmB_6 behaves analogously.[19]

Figure 17 shows a typical temperature course of the resistivity for another group of IV compounds in the example of $CeAl_3$.[171] In this group of substances, the resistivity is generally metallic in nature. However, it is often nonmonotonic, possessing maxima and minima. In $CeAl_3$ it vanishes as $T \to 0$ according to the law[16] $\rho(T) = BT^2$ characteristic of interelectronic scattering or scattering by spin fluctuations (paramagnons). In general form, people associate the anomalous behavior of the resistivity in IV compounds with special scattering mechanisms that exist in these states:
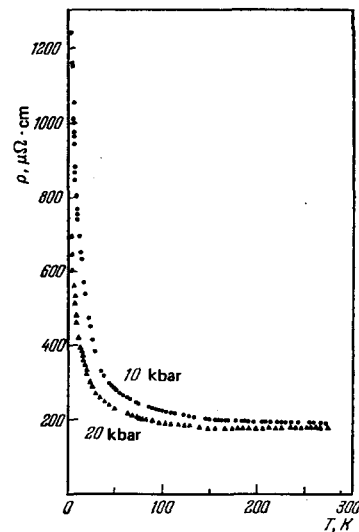

FIG. 15. Change in Mössbauer spectra with temperature. a) Eu_3S_4[25] (inhomogeneous IV); b) $EuRh_2$[43] (homogeneous IV).

FIG. 16. Temperature variation of the resistivity of SmS in the intermediate-valency phase.[143]
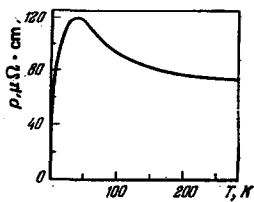
FIG. 17. Temperature-dependence of the resistivity in $CeAl_3$.[171]

scattering by slow charge and spin fluctuations. Here the fluctuations of charge (density) can also be accompanied by appreciable lattice changes (polaron effects; see Chap. 3, Sec. b, 5). As long as these fluctuations are incoherent, they will contribute to the resistivity. This mechanism, which explains the increased resistivity with decreasing temperature, is essentially closely connected with the Kondo mechanism (we recall that the value of the Kondo temperature itself is large in these systems). Establishment of coherence at low temperatures turns off this scattering mechanism. Apparently this is observed in $CeAl_3$.

The existence in IV phases of additional scattering mechanisms is confirmed by direct experiments. In the dielectric-metal transition in SmS, the mobility of the carriers declines by a factor of about 20.[60] Moreover, in the system $Sm_{1-x}Y_xS$, the conductivity even *declines* in the transition with valency change (transition from the "black" semiconductor to the "golden" metallic modification).[153] Actually, here at a concentration below the critical, a metallic-type conduction already exists, evidently caused by flow of electrons through the impurity system.

The examples presented pose an entire set of questions. First of all, in SmS and SmB_6 the resistivity continues to increase down to the lowest studied temperatures as though the electronic spectrum contained a gap. The existence of this small gap was proposed by Mott.[154] However, it seems to contradict the optical properties, and in particular, the linear trend of the heat capacity. At least, even if some type of gap exists in the spectrum, it cannot have a single one-particle character.

One of the possible explanations of such behavior in SmS and SmB_6 might be the effect of defects: in a system having a narrow peak in the density of states at E_F (of width $\lesssim 10^2$ K) and with strong correlations, the effect of even a relatively weak disorder might be very large and lead to Anderson localization of electrons. Kasuya[19] has proposed this explanation as applied to SmB_6, where the system is known usually to contain many vacancies (up to 15%). The hypothesis of the existence in the metallic phase of SmS and SmB_6 of static Sm^{3+} ions ("impurities") has also been adduced to explain the increase in resistivity with decreasing temperature in these compounds. These ions might give rise to such behavior owing to scattering by their magnetic moment (the Kondo effect).[155] Chui[159] has explained the increased resistivity in SmS and SmB_6 by exciton effects of the type discussed in Chap. 3. On

the whole, the situation with these compounds remains unexplained.[156]

A number of problems arise also in systems of the type of $CeAl_3$. Estimates of the Fermi temperature for $CeAl_3$ from the values of the electronic heat capacity and the susceptibility give values $T_F = 25.3$ and 15.6 K. If we estimate the degeneracy temperature from the coefficient B in the formula $\rho = BT^2$, we get $T_F = 2.7$ K (Ref. 16), an even lower value. It is not yet clear what type of coherent ground state is realized as $T \to 0$, nor what properties such a Fermi fluid might possess. We note only that peaks have been found in the heat capacity of $CeAl_3$ at $T \sim 3-6$ K, and that this region shows anomalies of certain other properties.[158]

We mention also that interesting effects have been found in a number of other kinetic characteristics of IV systems. Thus, in some cases a negative magnetoresistance has been found and is sometimes considerable.[157] Anomalies have been found in tunneling in IV substances (e.g., $YbCu_2Si_2$ shows[7] a peak at zero bias with a very large amplitude of 77% and with a half-width of 7.5 meV), and the behavior of the Hall effect is usually complicated.[3] All these data again show that the existence in IV systems of an energy structure having a characteristic energy of the order of 10–100 K is clearly manifested in all the properties of these substances in the accessible region of temperatures, pressures, magnetic fields, etc.

5. CONCLUSION. FUNDAMENTAL PROBLEMS

In summarizing the treatment of the properties of IV states, let us discuss what conclusions we can draw from the known facts about the structure and properties of the ground state of these systems, and what problems they pose for further studies.

In the first stage, the properties of IV states have been studied mainly for the model of an isolated impurity. We have often used this approach in this review. At present the situation has become sufficiently clarified on this level. It is evident, at least qualitatively, that even a single impurity can have properties typical of an IVS: in the case in which the position of the f level E_0 is close to the Fermi level, the occupation of the f level is nonintegral, a high density of states arises at the Fermi surface, the system goes over at low temperatures into a nonmagnetic state, a narrow resonance directly at the Fermi surface can give rise to a strong scattering mechanism, etc. This situation is described by the asymmetric model of Anderson (possibly having to include other interactions[94]) and it has many properties typical of the Kondo effect (slow spin fluctuations, strong coupling). Moreover, in addition to the spin fluctuations, slow charge fluctuations also occur in this case,[94] with respect to which the system also behaves as a Kondo system.[161]

Although there is as yet no complete mathematical study of the problem of a single impurity, qualitatively its fundamental properties are nevertheless known. The center of gravity of the IV problem has now shifted

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to studying the *interaction* of centers under IV conditions. All of the collective effects and the properties of the ground state, just like the conditions for appearance of an IVS, hinge on this problem. The main problem is what type of ground state is realized in IV systems. The first possibility is a coherent state of the type of the Fermi fluid, but with an extremely low degeneracy temperature and with a large effective mass. The properties of a Fermi fluid with such low values of the characteristic energies are not clear: it would seem that when $T_F \sim 10$–100 K, practically all the interactions not taken into account thus far in discussion can prove substantial. In particular, the Coulombic interaction of the f electrons (or, better, of the f holes) at different centers might lead for such a low value of T_F to spatial ordering [of the type of Wigner crystallization or of the formation of an ordinary condensed state (solid or liquid) from heavy positive ions and electrons]. L. V. Keldysh has proposed such ideas (see also Ref. 114). Similar possibilities are mentioned also in Ref. 5. Electron-phonon interaction might also lead to analogous consequences (see Chap. 3, Sec. b, 5). Other mechanisms are also possible that lead to such a structure (e.g., the interaction between two Kondo impurities should depend on their separation, though it is not clear *a priori* whether it will be an attraction or repulsion).

The establishment in an IV phase of a spatially periodic structure of the type of a crystal of heavy f holes is counteracted by $f - s$ hybridization, which leads to a finite lifetime and to effective delocalization of the f electrons. It is not yet clear theoretically nor experimentally whether this factor suppresses spatial correlation completely and in what cases, or whether some fraction of it is conserved, nor whether hybridization is the only mechanism of this type.

Another problem (actually connected to the former) is the role played in IV states of electron-hole correlations of the exciton type. Owing to the large mass of the f electrons and the small effective width of the f level, these effects must apparently prove substantial. It is now known whether they will lead to formation of some coherent state of the type of an excitonic insulator nor whether a gap or a pseudogap arises in the spectrum.

One interesting problem is why many IV systems (SmS, SmB_6, $TmSe$) do not show in their conductivity a transition to Fermi-fluid behavior of the type found in $CeAl_3$, although they also possess a linear electronic heat capacity and they recall true metals in their optical properties. It is unclear whether this involves a fundamental different type of ground state or can be explained by some side factors, e.g., defects or Kondo impurities.

In principle, the properties of different IV compounds actually can differ. One of the possible differences has been noted in Refs. 11 and 156: whereas α–Ce and $CeAl_3$ contain many conduction electrons, in SmS and SmB_6 all the conduction electrons are electrons that have left the f level, so that their number equals the number of f holes. This can, for example, ease the

conditions for exciton pairing; here also the conditions for Wigner crystallization might be eased. If this is true, then we can suppose, for example, that $YbAl_3$ and $EuRh_2$ will be analogous in this regard to $CeAl_3$, while the metallic phases EuO and YbS will resemble SmS.

Another possibility is that the fundamental difference between SmS and $CeAl_3$ involves the difference in electronic structure of the corresponding ions.[160] In Ce the configurations $4f^0$ and $4f^1$ i.e., a completely filled shell and a shell with one f electron are in resonance. In this case intraatomic correlations of the Hund type play no role. In Sm the multielectron configurations $4f^5$ and $4f^6$ are essential, where such correlations play a fundamental role (both intraatomic exchange interaction and spin-orbital interaction prove larger for f electrons than the width Γ of the f level). This can somehow affect the type of ground state (e.g., by further decreasing the characteristic energy ω_{ICF} of the interconfigurational fluctuations as compared with $\Gamma = \pi \rho V^2$,[160] whereupon, for an even narrower band, the conditions are eased for Anderson localization or formation of a valency-density wave). From this standpoint we might expect that all the compounds of Yb, including YbS at high pressures, should be analogs of Ce [Yb^{2+} has a filled $4f^{14}$ shell, while Yb^{3+} ($4f^{13}$) has one hole in the f shell], whereas all substances containing Eu and Tm, including intermetallic compounds of the type of $EuRh_2$, will be closer to SmS and SmB_6. This would be interesting to test experimentally.

Another interesting problem, fortuitously or not, is that the characteristic times τ_{ICF} of the valency fluctuations coincide with the characteristic phonon times $\tau_{ph} = \hbar / \omega_{ph} \approx 10^{-13}$–$10^{-14}$ s.[119] Apparently this is not fortuitous. If the characteristic times τ_{ICF} were much larger than the phonon times, then the lattice would be able to relax in different ways around the centers having different valencies. In this case even a static distribution of the ions of differing valencies might be realized, i.e., the case of an inhomogeneous IV. On the other hand, the case $\tau_{ICF} \ll 10^{-13}$–10^{-14} s would correspond to an ordinary metal with a broad band and fast charge fluctuations. Usually in treating IV problems people emphasize that IV is observed when $|E_0 - E_F| \lesssim \Gamma$, i.e., in the intermediate case between the situation of a deep level, $E_0 \ll E_F$, and an empty level, $E_0 \gg E_F$. However, it seems that even as regards the electron-phonon interaction, IV compounds lie at the boundary between phases with averaged and with local deformations, and that the very existence of states with intermediate valency is closely connected with this circumstance.

Another point that perhaps might clarify the situation with IV phases is their analogy with states "inside" a phase transition, which we have discussed in Chap. 4, Sec. a. Many features of IV states (anomalously large compressibility and heat capacity, the important role of slow valency fluctuations and strong scattering by them) confirm the validity of this analogy. It is not yet clear how far it extends nor whether it can be realized more concretely in some way.

It is also worth discussing to what extent the concept

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of delocalized or localized electrons is applicable to IVSs. One can advance arguments that in an IV phase the states at the Fermi surface actually have a strong interaction. We can estimate it as follows. As is evident from the results of Chap. 3, when we include $f-s$ hybridization, the mean interaction $\bar{U}_{int}$ of the electrons is proportional to the contribution of the f electrons to the overall wave function, while the characteristic kinetic energy of the electrons at E_F is $\bar{T}_{kin} \approx 1/\rho_f(E_f)$. Using Eqs. (8) and (9) or the analogous relationships for the periodic case, we can easily convince ourselves that, when $|E_0 - E_F| \lesssim V$ and $0.1 \lesssim n_f \lesssim 0.9$ [see (10)], i.e., almost always in IV substances, we have $\bar{U}_{int} > \bar{T}_{kin}$. Thus IV states are characterized by strong interelectronic correlation (see, e.g., Refs. 1 and 2), or at best lie "at the boundary" of a Mott transition. Apparently the IV problem actually contains within itself all the difficulties of the problem of the Mott-Hubbard dielectric-metal transition.

We can say in summarizing that as yet it is not always really clear, even qualitatively, in what cases the properties of an isolated impurity "survive" on going to a concentrated system and how they change; what type of coherent ground state arises, and whether it is the same in different compounds; whether the ground state will be spatially homogeneous or whether a periodic structure will arise in it of the type of a Wigner crystal or valency-density waves; whether the energy spectrum will contain a gap (or pseudogap); in what cases the magnetic behavior will be analogous to Kondo behavior, and when magnetic ordering will arise: and what role lattice effects will play in the IVS. We can ask an even sharper question: is the ground state of IV systems ultimately simply an analog of an ordinary state of the type of the Fermi fluid, but with anomalous values of the parameters, or does it amount to something different? All these problems are extremely complicated, yet very interesting, and they evidently merit attention from both theoreticians and experimentalists.

Thus, as we see from the above, there are still many unsolved problems in the physics of IV states. This justifies the title of this review "The Problem of Intermediate Valency": though the general qualitative picture has been drawn, a problem actually exists. To a considerable extent this problem is a theoretical one (at present the physics of intermediate-valency compounds is a "heaven for experimentalists and a nightmare for theoreticians"). However, of course, very much here depends on the experimentalists.

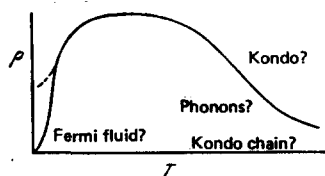The author finds it hard to forswear the pleasure of

FIG. 18. The problem of intermediate valency according to Anderson[164] (cf. Fig. 17).
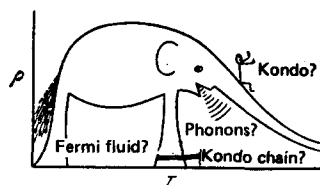

FIG. 19. Same as Fig. 18.[164]

presenting in closing another formulation of the IV problem due to Anderson.[164] In illustrating this problem with one of the clearest examples, CeAl$_3$, Anderson gave the curve of the resistivity of CeAl$_3$ in the following form, Fig. 18, while marking on it certain physical factors and phenomena that had been adduced to explain the behavior of the corresponding regions of the curve. In connection with it he recalls the Indian parable of the seven blind wise men and the elephant: One touched the elephant's leg and said that the elephant is a large tree, another studied the tail and said that it is a rope, a third said that it is a fan, etc. Upon stating that the current approach to the IV problem often reminds him of this parable, Anderson "materialized" it in the following form (Fig. 19). In the language of "Anderson's elephant", the formulation of the fundamental problems sounds about like: a) Where did the elephant come from, i.e., when and why do IV states arise? b) Why doesn't it run away, i.e., what stabilizes these states? c) What does it amount to, etc. There is a hope that, if we get even partial answers to these questions, we shall be able to learn something, not only about the elephant itself, but also about other, perhaps less exotic, though no less interesting and important and more widespread "beasts".

In closing I express my sincere gratitude to L. V. Keldysh, whose discussions have facilitated the development of the views reflected in this review.

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