

## Intermediate Valence State of Cerium in Intermetallics

Wojciech Suski

*Polish Academy of Sciences, W. Trzebiatowski Institute of Low Temperature and Structure Research,  
P.O. Box 1410, 50-950 Wrocław 2, Poland*

*and International Laboratory of High Magnetic Fields and Low Temperatures, ul. Gajowicka 95, 53-421 Wrocław, Poland*

(Received July 12, 1999)

**Ce exhibits the intermediate valence (IV) state both as an element and in its compounds. In the present review characteristic behavior of the materials showing the IV state are described. Then the methods of producing this state : the application of the external pressure, temperature and magnetic field as well as the alloying are being discussed. An identification of the IV state is frequently not a simple goal and the best results can be obtained using a combination of various independent methods. Particular attention is paid to the X-ray spectroscopy, lattice parameters and the magnetic properties. As the examples of the IV state in the Ce compounds the properties of following materials are reported: CeRhSb, CeCu<sub>5</sub>In<sub>7</sub>, CeAg<sub>6</sub>In<sub>6</sub>, Sc<sub>1-x</sub>Ce<sub>x</sub>Fe<sub>4</sub>Al<sub>8</sub> and for comparison Sc<sub>1-x</sub>Yb<sub>x</sub>Fe<sub>4</sub>Al<sub>8</sub>.**

### 1. Introduction

The phenomena of the intermediate valence state (IV) was detected for the first time in the Joffe Institute in St. Petersburg during an examination of the magnetic semiconductors: the samarium monochalcogenides [1]. It was observed that these materials change their colour under small pressure. The investigations of the electrical resistivity have shown that also under pressure, different for different chalcogenides there is a transition to the metallic state [2]. This transition is accompanied by a decrease of the lattice parameters. It has been explained that under an applied pressure one electron being promoted from the narrow  $f$  level to the conduction band, is delocalized. Very soon it was observed that the IV state is observed not only in the Sm ion, resulting from the transition:  $\text{Sm}^{2+} \rightarrow \text{Sm}^{3+} + e^-$ , but also in other lanthanide ions listed in Table 1. It follows from this Table, that the IV state is common for the ions with the electronic configurations close to the particularly stable  $f^0$ ,  $f^7$  and  $f^{14}$  ones. Also the authors of [3] claim that under high pressure the IV state is induced in Pr. In the Table there are shown two valence states of each ion but the valence observed in their compounds is intermediate between both due to a quantummechanical hybridization. For the described phenomena the term "valence fluctuations" was also applied, however, it suggests a dynamic process and is derived from the early assumption that there exist "fast" and "slow" measurements relative to an intrinsic charge fluctuation between the two valences in question. In fact the quantummechanical ground state of an IV system at  $T = 0$  is by definition static. Since typical measure-

ments like X-ray photoemission spectra (XPS) or Mössbauer effect (ME) are considered fast and slow, respectively, but are largely temperature independent for these materials they would yield the same results at  $T = 0$  thus invalidating the fluctuating picture [4]. Beside the materials in which each cation has the same but not integer valence there exist also classical mixtures of different but integer valences related to the ions occupying various but determined crystallographic positions. These compounds are called inhomogeneously mixed valence materials. But they are not a subject of the present review.

The IV state can occur under various conditions. In some materials this state is stable under ambient pressure and room temperature. In others the IV state can be induced by external pressure, chemical pressure or alloying and temperature. This last factor is relatively rarely the reason for creation of the IV state.

Table 1. Lanthanides exhibiting the IV state

Element	electronic configuration	valence
Ce	$4f^{15}d^16s^2$	3
	$4f^{05}d^26s^2$	4
Sm	$4f^{65}d^06s^2$	2
	$4f^{55}d^16s^2$	3
Eu	$4f^{75}d^06s^2$	2
	$4f^{65}d^16s^2$	3
Tm	$4f^{135}d^06s^2$	2
	$4f^{125}d^16s^2$	3
Yb	$4f^{145}d^06s^2$	2
	$4f^{135}d^06s^2$	3

Table 2. Methods of identification of the IV state [7]

Method	XRD	volume thermal expansion	Mössbauer effect	$L_{III}$ X-ray absorption	XPS UPS	static susceptibility
ionic species	all	all	Eu, Sm, Tm, Yb, Np	all	all	all
dynamic or static	no	possible	yes	no	possible	yes
pressure range, GPa	0-40	0	0-5	0-40	0	0-4.5
temperature, K	1-1000	1-400	0.01-700	1-300	77-300	1-1200
relative accuracy	$10^{-2}$	$<10^{-4}$	$10^{-2}$	$10^{-1}$	$10^{-1}$ - $10^{-2}$	$10^{-1}$
Problems :	a) calibration of $a_{n+1}$ , $a_n$		calibration of $\delta_{n+1}$ , $\delta_n$		final state effect	a) bulk valence
	b) is valence linear in $(a_{n+1}, a_n)$ ?					b) final state effects
						only at $T \gg T_f$

It is an interesting question why only  $4f$  materials exhibit intermediate valence. As it is broadly known some of the actinide compounds ( $5f$ ) are reported to be heavy fermion ( $UPt_3$ ,  $UBe_{13}$ , etc.). Wachter [4] claims that heavy fermions are also intermediate valent although the apparent valence of uranium in them is nearly integer. The uranium monochalcogenides, particularly  $USe$  and  $UTe$ , provide a convincing indication of the IV, however, they also show ferromagnetic order, which generally is not typical for IV. This statement might be generally not valid as shown by Nolting and Ramakanth [5]. As regards the  $d$  materials some indication of the IV state is reported for the V compounds, but it seems that such a state can be expected for the Mn and Cr compounds, too. Wachter [4] suggests that the new high  $T_c$  compounds of the type  $YBa_2Cu_3O_7$  not only are mixed valent regarding  $Cu^{2+}$  and  $Cu^{3+}$  ions but also intermediate valent. A definite experimental evidence, however, is still missing.

Perhaps, the most advanced theory explaining the IV state is the hybridization gap model (see e.g. [4]) but the author of the present review, being an experimentalist, is not going to the details, referring rather to original papers.

## 2. Experimental

Below we present the methods of an identification of the IV state. As mentioned above, already in the first papers devoted to the IV state, the change of colour has been reported for the Sm monochalcogenides as an indication of the valence transformation. The methods presented in Table 2, although listed some years ago are still important for the identification of the IV state. The simplest method of determination of valence is from the lattice parameters. However, an application of this method raises some problems:

a. As the result of stresses in the crystal lattice following a change of valence the dependence of specific volume on the valence for the lanthanide compounds is nonlinear.

b. The additional compression of the crystal lattice follows the configurational mixing. Then the relation between specific volume and valence is described by the equation [6]:

$$V(n + v) = (n + v) / [(1-v) n / V_n + v(n + 1) / V_{n+1}],$$

where  $n$  and  $v$  are the fractional (intermediate) valence,  $V_n$  and  $V_{n+1}$  specific volume of the compounds with  $n$  and  $(n + 1)$ -valence.

c. Frequently the specific volume change results from the special type of chemical bonding. This fact causes the discrepancy between the valence determined from the lattice parameters, the Mössbauer effect and XPS. Moreover, it is suggested that the change of the lattice parameters results also from the crystal field (CEF) effects.

The methods listed in Table 2 [7] provide a firm indication of the IV state, but this Table does not contain all available methods and effects. For example, a jump of the electrical resistivity accompanying the metal-semiconductor transition or the specific temperature dependence of the coefficient of the Hall effect. However, this last effect is observed only occasionally. It should be pointed out that none of the presented methods does give the fully convincing indication of the IV state. The final conclusion can be presented only after several experiments.

## 3. Results and Discussion

As regards the static magnetic susceptibility,  $\chi$ , the temperature of the setup of the IV state can be related to the maximum in  $\chi(T)$  [8]. The contribution to the paramagnetic Curie temperature has been calculated for the various IV rare earth ions [9]. Moreover, in majority of the IV ions one valent form exhibits localized magnetic moment, whereas the other one is nonmagnetic (diamagnetic or temperature independent paramagnetic). Therefore, the measured magnetic moment should give an indication of the valence state, moreover, that the CEF effects are only a small perturbation for the lanthanide ions. Single exception are the Tm ions which both exhibit magnetic moments, which exclude possibility of using the magnetic moment value for the determination of the Tm valence in its compounds.

Below we present an indication of the IV state of Ce in some intermetallics. Majority of these materials have been examined with the contribution of the present author.

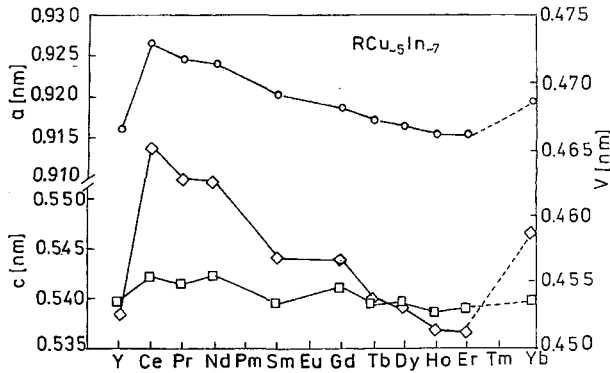


Fig. 1. Lattice parameters  $a$  and  $c$  and unit cell volumes,  $V$ , for the  $\text{LnCu}_5\text{In}_7$  compounds [15].

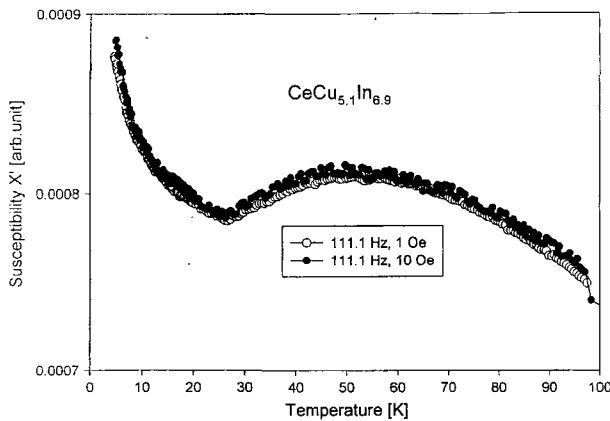


Fig. 2. Real part of ac magnetic susceptibility,  $\chi_{ac}$ , of  $\text{CeCu}_5\text{In}_7$  versus temperature [16].

$\text{CeRhSb}$  has been reported in many papers as a heavy fermion system. Determined by Malik and Adroja [10] the unit cell volumes of the  $\text{LnRhSb}$  type compounds for light lanthanides show the deviation from a smooth curve for Ce antimonide suggesting the IV state. Perhaps the most extended paper devoted to this problem has been published by Slebarski *et al.* [11]. They found the effective magnetic moment at 300 K,  $\mu_{\text{eff}} = 2.1 \mu_B/\text{f.u.}$ , which is less than the Hund's rule value of the free ion  $\text{Ce}^{3+}$ . There could be various reasons for this discrepancy. As at 1.5 K, free carriers do not compensate the local magnetic moment due to the local Kondo interaction, the CEF interaction in the IV state can decrease the magnetic moment. In favour of the second hypothesis an adequate description of the temperature dependence of the magnetic susceptibility in the term of the ionic two-level interconfigurational fluctuation model (ICF) model can be considered. However, the  $\chi(T)$  plot does not show any maximum, characteristic for the IV system. In the Ce 3d XPS spectra three final-state contributions  $f^0$ ,  $f^1$  and  $f^2$  are observed. The  $f^2$  components are attributed to the hybridization between the  $f$  states and the conduction band. The other two are a clear evidence for the IV state, although no detailed interpretation of the spectra is attempted because of the strong multiplet splittings.

We have devoted a considerable effort to examine the

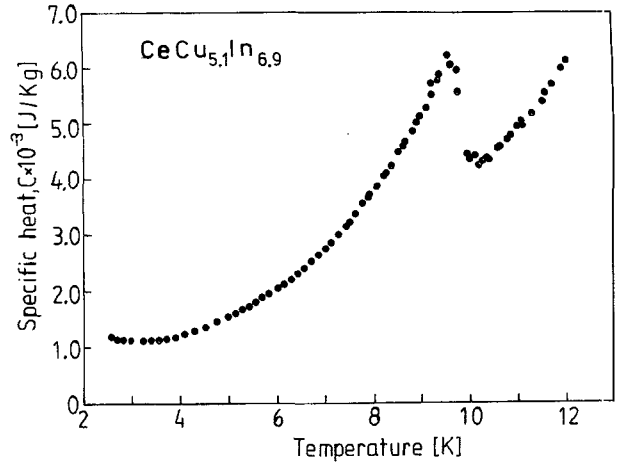


Fig. 3. Specific heat of  $\text{CeCu}_5\text{In}_7$  versus temperature (according to A. Czopnik).

intermetallic ternaries with the tetragonal  $\text{ThMn}_{12}$  type structure [12]. Among them some of the Ce or U compounds are suspected to be the IV or HF systems. For example, the  $\text{UCu}_{4+x}\text{Al}_8$  system depending on  $x$  can exhibit the Landau heavy fermion liquid versus non-Fermi liquid behavior [13]. However,  $\text{CeAg}_4\text{Al}_8$  does not exhibit superconductivity, magnetic order or the HF state [14]. The presented in Fig. 1 lattice parameters  $a$  and  $c$ , and unit cell volumes  $V$  vs.  $Z$  plot for the  $\text{LnCu}_5\text{In}_7$  compounds [15] exhibits clear anomalies for the Yb and Ce compounds. However, this last anomaly does not correspond to the presence of the Ce ion with valence  $3 + \delta$ , because in this case the lattice parameters etc should be smaller. The absence of the La compound makes this statement slightly doubtful. In Fig. 2 [16] the ac magnetic susceptibility of  $\text{CeCu}_5\text{In}_7$  versus temperature is shown. It can be noticed that there is a maximum in  $\chi_{ac}(T)$  plot at about 50 K. According to [8] it is not the thermodynamic but effective temperature:  $T_{\text{eff}} = T + T_{\text{sf}}$ . In this case it can be expected that  $T_{\text{sf}}$  is that observed in the  $C(T)$  plot at 9.5 K and shown in Fig. 3. For the final conclusion the XPS experiment is badly needed.

In Fig. 4 there are the lattice parameters of the  $\text{LnAg}_6\text{In}_6$  presented. These compounds are obtained for light lanthanides only and their lattice parameters do not present any regularity, even the lanthanide contraction [17] and there-

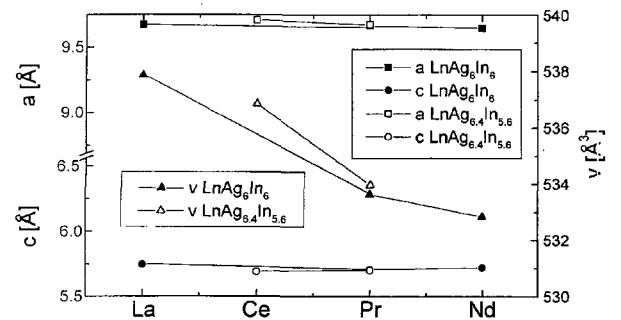


Fig. 4. Lattice parameters  $a$  and  $c$  and unit cell volumes,  $V$ , for the  $\text{LnAg}_6\text{In}_6$  compounds [17].

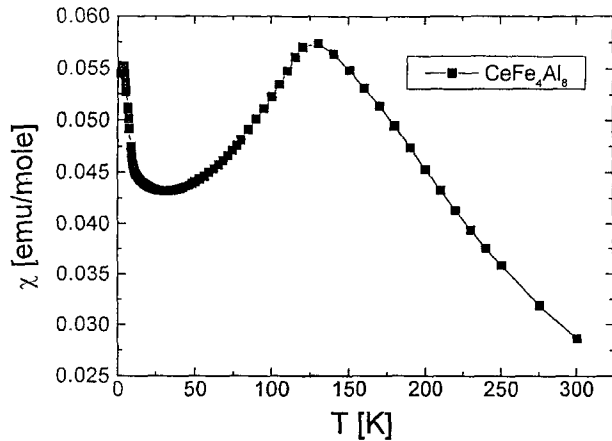


Fig. 5. Magnetic susceptibility,  $\chi$ , versus temperature for  $\text{CeFe}_4\text{Al}_8$  [20].

fore also the lattice parameters of  $\text{CeAg}_{6.4}\text{In}_{5.6}$  cannot be considered as an indication of the IV state. The temperature dependence of the magnetic susceptibility of this compound also does not exhibit any anomaly. The low temperature specific heat does not show any anomaly, too. However, a lack of magnetic ordering and a strange stoichiometry of this material were considered in [17] as possible hints for the IV state.

Now we discuss the  $\text{Sc}_x\text{Ce}_{1-x}\text{Fe}_4\text{Al}_8$  system. In pure  $\text{CeFe}_4\text{Al}_8$  the cerium ion is in the IV state with  $\nu = 3.28(5)$  as it was proved by Shcherba *et al.* from the XPR [18] and  $L_{\text{III}}$  XAS [19] experiments. This opinion is confirmed by the unit cell volume versus  $Z$  plot for the  $\text{LnFe}_4\text{Al}_8$  family. It can be observed that there is a clear anomaly for  $\text{CeFe}_4\text{Al}_8$ . However, the temperature dependence of the magnetic susceptibility is difficult to interpret in term of the IV state because of the AF order in the Fe sublattice. The presented in Fig. 5  $\chi_m(T)$  plot [20] in fair agreement with [19, 21, 22], demonstrates a maximum at 130.2 K related to the mentioned earlier AF order, and the second maximum at 3.25 K not found previously. At present we do not know the reason for this maximum. The dilution of  $\text{CeFe}_4\text{Al}_8$  by Sc which has a smaller metallic radius than Sc is aimed to check if such a procedure can induce a further change of valence.

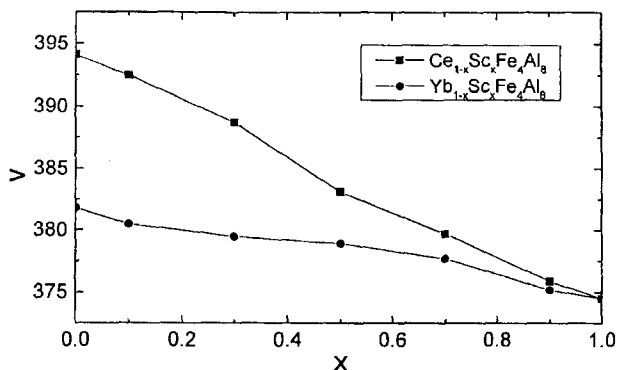


Fig. 6. Unit cell volumes,  $V$ , versus Sc concentration,  $x$ , in the  $\text{Ce}_{1-x}\text{Sc}_x\text{Fe}_4\text{Al}_8$  and  $\text{Yb}_{1-x}\text{Sc}_x\text{Fe}_4\text{Al}_8$  alloys [20].

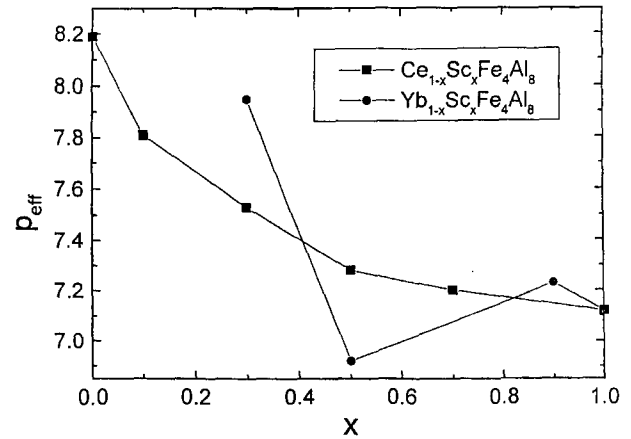


Fig. 7. Effective magnetic moment,  $p_{\text{eff}}$  versus Sc concentration,  $x$ , in the  $\text{Ce}_{1-x}\text{Sc}_x\text{Fe}_4\text{Al}_8$  and  $\text{Yb}_{1-x}\text{Sc}_x\text{Fe}_4\text{Al}_8$  alloys [20].

The unit cell volumes,  $V$ , versus Sc concentration,  $x$ , in the  $\text{Ce}_{1-x}\text{Sc}_x\text{Fe}_4\text{Al}_8$  and  $\text{Yb}_{1-x}\text{Sc}_x\text{Fe}_4\text{Al}_8$  alloys are shown in Fig. 6 [20]. In both systems  $V$ s decrease with increasing Sc concentration in full accord with the substitution of a larger atom by a smaller one. In case of the Yb compounds the change of valence from  $\text{Yb}^{3+}$  [18, 19] toward  $\text{Yb}^{2+}$  should result in an increase of  $V$  but opposite observation follows from Fig. 6. We cannot decide at present if the decrease of  $V$  in the case of the Ce alloys is solely due to the effect of substitution or also to the contribution of valence increase towards more tetravalent ion. It seems that the  $p_{\text{eff}}(x)$  plot for both systems presented in Fig. 7 proves that the valence of both Ce and Yb does not change.

#### 4. Conclusion

In conclusion, the IV state for numerous Ce intermetallics can be proposed, however, various experiments give different, frequently contradictory results. This situation needs further experiments, particularly the X-ray photoemission on extremely clean samples, with exactly determined surface conditions (oxygen free). Single crystal samples are particularly needed.

#### References

- [1] V. P. Zhuze, A. V. Golubkov, E. V. Goncharova, T. I. Komarova, and V. M. Sergeeva, *Fiz. Tverd. Tela* **6**, 268 (1964).
- [2] A. Jayaraman, V. Narayamurthi, E. Bucher, and R. G. Maines, *Phys. Rev. Lett.*, **25**, 1430 (1970).
- [3] W. A. Grosshans, Y. K. Vohra, and W. B. Holzapfel, *J. Phys. F: Metal Phys.*, **13**, L147 (1983).
- [4] P. Wachter, in: *Handbook on the Physics and Chemistry of Rare Earths*, vol. 19, ch. 132, ed. by K. A. Gschneidner, Jr., L. Eyring, G. H. Lander, and G. R. Choppin (North Holland, Amsterdam 1993) p. 1.
- [5] W. Nolting and A. Ramakanth, *Phys. Rev.*, **B 23** (1986) 1838.

- [6] G. Neumann, H. Pott, J. Rohler, W. Schlabitz, and H. Zahel, in: *Valence Instabilities*, ed. by P. Wachter and H. Boppart (North Holland, Amsterdam 1982) p. 87.
- [7] D. Wohlleben, in: *Valence Fluctuations in Solids*, ed. by L. M. Falicov, W. Hanke, and M. B. Maple (North Holland, Amsterdam 1981) p. 1.
- [8] B. C. Sales and D. Wohlleben, *Phys. Rev. Lett.*, **35**, 1240 (1975).
- [9] E. Müller-Hartmann and Y. Kuramoto, *Z. Phys.*, **B 52**, 211 (1983).
- [10] S. K. Malik and D. T. Adroja, *Phys. Rev.*, **B 43**, 6277 (1991).
- [11] A. Slebarski, A. Jezierski, A. Zygmunt, S. Mähl, and M. Neumann, *Phys. Rev.*, **B 58**, 13 498 (1998).
- [12] W. Suski, in: *Handbook on the Physics and Chemistry of Rare Earths*, vol. 22, ch. 149, ed. by K. A. Gschneidner, Jr. and L. Eyring (Elsevier, Amsterdam 1996) p. 143.
- [13] T. Nishioka, Y. Kurakashi, R. Fukuda, and M. Kotani, *Czech. J. Phys.*, **46**, 2065 (1996).
- [14] U. Rauchschwalbe, U. Gottwick, U. Ahlheim, H. M. Meyer, and F. Steglich, *J. Less-Comm. Met.*, **111**, 265 (1985).
- [15] L. V. Sysa, Ya. M. Kalychak, Bakar Akhmed, and V. N. Baranyak, *Kristallografia* **34**, 744 (1989).
- [16] A. Zaleski private communication.
- [17] V. I. Zaremba, Ya. M. Kalychak, Ya. V. Galadzhun, W. Suski, and K. Wochowski, *J. Solid State Chem.*, **145** (1999) in press.
- [18] I. D. Shcherba, I. I. Kravchenko, M. D. Koterlin, A. P. Kushnir, and A. P. Shpak, *Metallofizika* **14**, 3 (1992).
- [19] I. D. Shcherba, M. D. Koterlyn, A. P. Kushnir, R. R. Kutjanskyj, V. G. Synjushko, Yu. D. Tsybukh, B. M. Yatsyk, and I. I. Margolych, *J. Magn. Magn. Mater.*, **157-158**, 688 (1996).
- [20] W. Suski, K. Wochowski, and B. Kotur, *Physica B* (1999), submitted.
- [21] K. H. J. Buschow and A. M. van der Kraan, *J. Phys. F: Metal Phys.*, **8**, 921 (1978).
- [22] I. Felner and I. Nowik, *J. Phys. Chem. Solids* **39**, 951 (1978).