

MAGNETIC AFTEREFFECT OF INTERSTITIAL OXYGEN IN IRON*

M. FÖLDEAKI**, M. STEFÁN***, P. VOLTÁNIK****, K. LAZAR*****

Dynamical magnetic aftereffect and disaccommodation measurements were carried out on oxygen-alloyed and oxygen-free iron samples to prove the interstitial behaviour of oxygen as supposed on the basis of theoretical calculations. On oxygen-alloyed samples relaxations due to interstitial oxygen were found with parameters agreeing well with the calculated ones. Besides these processes, relaxations due to C—O pairs were also found with a very large pair binding energy. The effect of the alloying elements on the relaxations was also examined: in the presence of Ti (max 600 ppm) all these relaxations disappeared; in the presence of Al (max 150 ppm) the relaxation due to free interstitial oxygen disappeared, but the C—O pair relaxation did not.

МАГНИТНАЯ РЕЛАКСАЦИЯ ВНЕДРЕННОГО В МЕЖДОУЗЛИЕ КИСЛОРОДА В ЖЕЛЕЗЕ

В работе описаны эксперименты по определению динамического магнитного послепдействия и другие измерения на образцах железа с примесью и без примеси кислорода с целью доказательства свойств внедрения у кислорода, которые предпологались, исходя из теоретических расчетов. В образцах с примесью кислорода была обнаружена релаксация, обусловленная внедренными в междоузлие кислородом, параметры которой хорошо согласуются с расчетными. Кроме этих процессов, были обнаружены релаксации, обусловленные C—O парами с очень большой энергией связи пар.

Было также обнаружено влияние леггирующих элементов на релаксацию: в присутствии Ti (макс. 600 миллионных частей) все эти релаксации исчезают; в присутствии Al (макс. 150 миллионных частей) релаксация, обусловленная внедренным в междоузлие кислородом, исчезает, однако релаксация C—O пар не исчезает.

* Dedicated to Academician Vladimir Hajko on the occasion of his 60th birthday.

** Research Institute for Ferrous Metallurgy, BUDAPEST, Hungary.

*** Szepel Iron and Metal Works, BUDAPEST, Hungary.

**** P. J. Šafárik University, KOŠICE, Czechoslovakia.

***** Central Research Institute for Physics, BUDAPEST, Hungary.

I. INTRODUCTION

I.1. The magnetic aftereffect [1]

Time effects of magnetization due to the interaction of domain walls and crystal defects are called magnetic aftereffects.

Two main types of investigation are known: — the dynamical magnetic aftereffect measurement, where the real and/or imaginary part of the susceptibility is measured as a function of temperature; it can be described by the Debye functions —; the disaccommodation measurement, where the change of the susceptibility is measured as a function of the time elapsed after demagnetization.

I.2. The interstitial oxygen

To prove the interstitial behaviour of oxygen in iron, thermodynamical calculations were first carried out by Frank et al. [2]. Physical methods for an experimental verification were also discussed there. The magnetic aftereffect — being an extremely sensitive tool in the investigation of interstitials — was recommended first of all. The calculated values of the parameters to be measured are:

- the activation energy (kJ/mole): 94.3 ± 9.6
- the range of temperature recommended for disaccommodation measurements: $T[\text{tr}(T) \sim 10 \text{ min}] = 280 \pm 30 \text{ K}$
- the characteristic temperature of the dynamical magnetic aftereffect: $T_0 = 445 \pm 45 \text{ K}$ at 1000 Hz.
- the expected amplitude of the relaxation in both measurements: $\Delta\chi/\chi \leq 2\%$.

Although these calculations are ten years old, no experimental results have been published. As we have already reported, an aftereffect due to oxygen was found in oxygen alloyed pure iron samples [3] but the temperature region and the relaxation differed from the calculated values. Lately this effect has been investigated in detail and other relaxations at lower temperatures have been found [4].

II. EXPERIMENTAL PROCEDURE

II.1. Sample preparation

The samples were made from high purity iron at the Csepel Works. They were cold drawn to wires of 1 mm diameter. The chemical analysis of the samples is shown in Table 1.

Table 1

Sample	Composition of the samples in wt ppm				
	C	N	O	Ti	Al
Φ -Fe	20	10	50	20	10
1-Fe-Ti	51	10	47	215	40
3-Fe-Ti	49	16	44	600	70
6-Fe-Al	49	19	208	30	150
7-Fe-Al	46	15	97	30	90

As controlled by magnetic aftereffect measurements, no interstitial remained in solution after a slow cooling from 875 °C. To produce interstitial oxygen, the sample was kept in vapour saturated hydrogen at 875 °C for 4.5 hours, and quenched in silicone oil.

This treatment was done at the Central Research Institute for Physics.

II.2. Dynamical magnetic aftereffect measurements

During the measurement the magnetization of the heated sample was kept constant by varying the magnetizing field. The necessary change of the magnetizing field is proportional to the real part of the reciprocal susceptibility (r) due to aftereffect. The relative change $\Delta r/r_0$ (r_0 is the unrelaxed reciprocal susceptibility) as a function of T^{-1} , the reciprocal absolute temperature, is described in the ideal case by the following formula neglecting the distribution of the relaxation times¹⁾:

$$\frac{\Delta r(1/T)}{r_0} = \frac{(\Delta r/r_0)_{\max}}{1 + \exp \left[\frac{2Q}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right]}, \quad (1)$$

where Q is the activation energy, R the universal gas constant, T_0 the inflexion point (characteristic) temperature, $\Delta r(1/T)$ was measured for every 2K

¹⁾ If the distribution of the relaxation times cannot be neglected (this is the general case in a real material), then the aftereffect is described with the following integral, as the relaxation times follow the Gauss distribution:

$$\frac{\Delta r(1/T)}{r_0} = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} e^{-x^2} \frac{dx}{1 + \exp \left[2 \left[\frac{Q}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) + \beta x \right] \right]}, \quad (1a)$$

where β is the distribution parameter (for further details see: Nowick, A. S., Berry, B. S.: *Anelastic relaxation in Crystalline Solids*. Materials Science Series, Academic Press, New York—London, 1972).

temperature increase. The measurements were carried out at 10 and 1000 Hz. The activation energy was determined from the difference in the position of the inflexion points.

II.3. Disaccommodation measurements

The mutual-inductance of two coils containing the sample was measured by a complex bridge as a function of the time elapsed after demagnetization, as described by Vojtaník et al. [5]. The activation energy of the process was determined from the temperature dependence of the relaxation time.

III. EXPERIMENTAL RESULTS

III.1. Dynamical magnetic aftereffect

The Φ -Fe sample. The measurements were carried out on oxygen alloyed samples, and on interstitial-free slowly cooled samples. This background turned out to be linear and it was subtracted from the relaxation curve. The resulting curve is shown in Fig. 1, in the lower part (a).

The relaxation spectrum is very complicated. It was analysed in the following way: as shown in Table 1, the sample contains 20 wtppm carbon, which must be still in solution after the oxidizing heat treatment and quenching. Therefore the carbon relaxation corresponding to this interstitial quantity was subtracted from the relaxation; the resulting curves are shown Fig. 1, in the upper part (b). It was supposed in this calculation that the interstitially dissolved oxygen does not influence the aftereffect of the free interstitial carbon; due to small solubility of oxygen in iron this is very probable. The resulting curves consist of two relaxations at both frequencies; the starting points of the second processes are marked by

²⁾ The relaxation of the carbon was taken into consideration by means of the computer analysis in the following way: 1st step: The measured curve was logarithmically transformed on the basis of the logarithmic transformation of eq. 1.:

$$\ln \left[\frac{\left(\frac{\Delta\chi}{T_0}\right)_{\text{meas}} - 1}{\left(\frac{\Delta\chi}{T_0}\right)} \right] = \frac{2Q}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (1b)$$

This curve is linear if there is one component process present, and its point of intersection with the T^{-1} axis gives T_0 . If there is a two-component process present, the points from two lines, giving T_{01} and T_{02} at the intersections. 2nd step: Using eq. 1 and the T_{01} and T_{02} values, determined in the 1st step, the measured curve was fitted with two relaxation curves. The component curve corresponding to carbon was then subtracted from the measured curve; this result is given in the upper part of Fig. 1.

arrows, but when measuring at 1000 Hz this second process is covered by precipitation.

This high temperature aftereffect is not due to interstitial oxygen, therefore it will be discussed elsewhere. The inflexion points of the low temperature process were determined on the basis of Eq. 1b, and their values (marked by + on the curves of Fig. 1) are:

$$T_0(1000 \text{ Hz}) = 417 \text{ K} \quad T_0(10 \text{ Hz}) = 355 \text{ K.}$$

The activation energy calculated from these values is $Q = 91.3 \text{ kJ/mole}$. The pre-exponential factor is: $\tau_0 = 3.4 \times 10^{-15} \text{ sec}$. The amplitude of the relaxation is

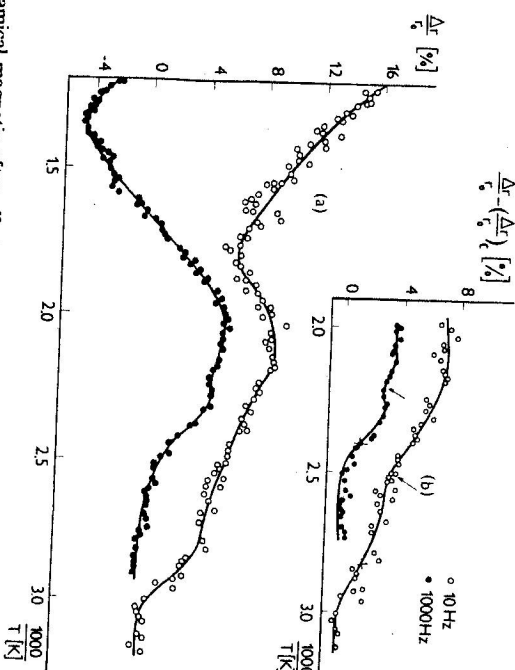


Fig. 1. Dynamical magnetic after effect curves of the Φ -Fe-O sample, after subtracting both the background (a) and the carbon relaxation (b).

3.2 and 2.6 %, at 10 and 1000 Hz, respectively. As the determined parameters of this relaxation agree well with the theoretically estimated values [2], it can be concluded that the relaxation is due to interstitial oxygen. The amplitude of the aftereffect is slightly higher than the calculated value; but in the calculations Frank et al. [2] have supposed that the proportionality factor between relaxation and solute atom concentration is the same for the oxygen and the carbon atoms. This factor is, however, different for different interstitials, e. g. for carbon and nitrogen [6]. Our measurement shows that this proportionality factor is 1.5 times greater for oxygen than for carbon. The difference in the amplitudes for 10 and 1000 Hz can be explained on the basis of Hejnal's results: [6] the relaxation amplitude is inversely proportional to the absolute temperature.

This alloy was heat-treated also in hydrogen containing less oxygen (half-saturated with vapour). In this case only one relaxation was found with the following parameters:

$$T_0(10 \text{ Hz}) = 340.9 \text{ K} \quad T_0(1000 \text{ Hz}) = 394.2 \text{ K}$$

$$\Delta = 3.4 \% \quad \Delta = 3.4 \%$$

$$Q = 95.5 \text{ kJ/mole} \quad \tau_0 = 3.2 \times 10^{-17} \text{ sec.}$$

The values show that no interstitial oxygen is present in this sample. The inflexion point temperatures are near to that of the interstitial carbon, but the higher activation energy and shorter pre-exponential factor suggest that this relaxation is strongly perturbed by oxygen, perhaps by the formation of C—O pairs. The amplitude of the relaxation is slightly higher than that of the interstitial carbon in the previous case; this can be very well explained by the lower decarburising effect of the gas containing less oxygen.

The amplitude of the relaxation is the same at 10 and 1000 Hz; this may be due to the following reasons:

a) The measurement at 1000 Hz was done first, and the amplitude of the aftereffect at 10 Hz corresponds to a precipitated state.

b) There is one more process present, (e.g. C—O pairs), which cannot be separated because of the small amplitude.

The 1-Fe-Ti; 3-Fe-Ti alloys. No aftereffect was found in this temperature region, indicating that no free interstitial is present in the sample.

The 6-Fe-Al alloy. As it is well known, the aluminium forms the stable ionic compound Al_2O_3 with oxygen. On the basis of the stoichiometric ratio of the compound and of the Al and O content of the raw material, all the aluminium present in this specimen is in the form of the Al_2O_3 compound. The parameters of the relaxation (only one was found):

$$T_0(10 \text{ Hz}) = 342.5 \text{ K} \quad T_0(1000 \text{ Hz}) = 393 \text{ K}$$

$$Q = 101.8 \text{ kJ/mole} \quad \tau_0 = 4.3 \times 10^{-20} \text{ sec.}$$

The parameters suggest that the relaxation is caused by the reorientation of interstitial pairs, namely C—O pairs. Free interstitial oxygen is not present in this sample. It is very probable that the oxidizing treatment was less effective in the presence of Al_2O_3 .

The 7-Fe—Al alloy. In this alloy free Al is also present. Curiously, both the aftereffect of interstitial oxygen and of carbon disappeared in this sample. The disappearance of interstitial oxygen can be interpreted by the presence of free Al and by the rapid forming of the stable ionic compound Al_2O_3 .

The carbon relaxation was probably broadened by the interaction with finely dispersed precipitates, and therefore covered by the background.

Summarizing the results, a dynamical magnetic aftereffect due to interstitial

Table 2

Low-temperature relaxations in samples containing oxygen					
Alloy	$T_0^{10 \text{ Hz}}$ (K)	$T_0^{1000 \text{ Hz}}$ (K)	Q (kJ/mole)	τ_0 sec	Physical meaning
Φ —Fe	355	417	91.3	3.4×10^{-15}	free oxygen
"more oxygen"	339	402	82.7	2.5×10^{-15}	free carbon
Φ —Fe "less oxygen"	341	394	95.5	3.2×10^{-17}	Perturbed interstitial C, and C—O pairs
6—Fe—Al	342	383	103.9	4.3×10^{-20}	Perturbed interstitial C, and C—O pairs
7—Fe—Al	no relaxation				no free interstitial
1—Fe—Ti					
3—Fe—Ti					

oxygen was found in oxygen-alloyed high purity iron; this has disappeared in samples containing additives (Ti, Al), which form stable compounds with oxygen. The parameters of the observed relaxations are summarized in Table 2.

To have more experimental verification, disaccommodation measurements were also carried out on the Φ —Fe and the 3—Fe—Ti samples.

III.2. Disaccommodation measurements

To find the temperature region where the measurement of the disaccommodation is possible, the permeability of quenched oxygen-free and oxygen alloyed samples was measured as a function of the temperature after Anagnostopoulos [7].

The susceptibility increases slowly with increasing temperature except in the temperature region where the disaccommodation can be measured; in this region the susceptibility remains constant or decreases (Fig. 2). It is well known that the effect below 270 K is due to carbon disaccommodation [6, 7].

In the region between 270—320 K the sample alloyed with oxygen has a different behaviour as compared to the oxygenfree sample. On the basis of Fig. 2, oxygen disaccommodation was investigated between 275—320 K. The amplitude of the disaccommodation was 2.5—3% when the measurements were begun and it decreased by about 20% when the bulk of the measurements was

carried out a month later. It seems that interstitial oxygen was rather sensitive to aging as the interstitial content decreased although the samples were kept in dry ice after quenching. On the basis of Hejnal's result [6], an amplitude of 3.9% would correspond to the dynamical magnetic aftereffect measurements. This discrepancy may be due to the following reasons:

1. Precipitation during the transportation from Budapest to Košice, where the measurements of the disaccommodation were carried out.
2. At the high temperature of the dynamical magnetic aftereffect there is more oxygen in solution (FeO starts to dissociate).
3. The proportionality factor between the amplitude of the aftereffect and the interstitial content is not the same in the two measurements.

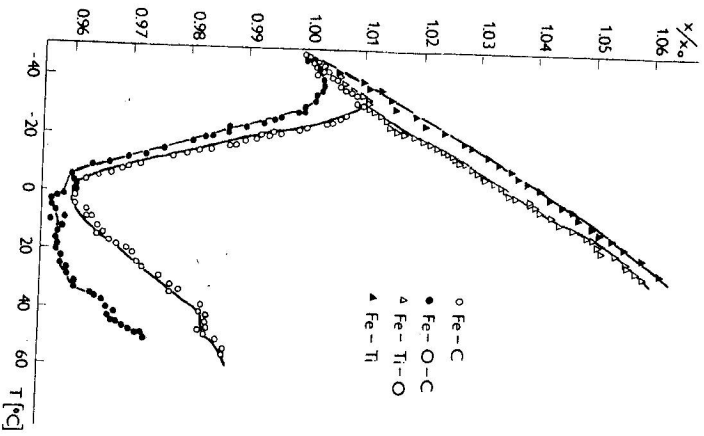


Fig. 2. Magnetic susceptibility of samples Φ -Fe-O-C; Φ -Fe-C and 3-Fe-Ti-O as a function of the temperature after demagnetization.

On the basis of physical reasons 1. is the most probable, as it was shown that interstitial oxygen is — perhaps due to its small solubility — very sensitive to aging. A significant dissociation is not probable, because there is no discrepancy between the amplitudes of the aftereffect at 10 and 1000 Hz, in the case of a significant dissociation $\Delta_{1000\text{ Hz}} \gg \Delta_{10\text{ Hz}}$ would have been found.

No physical reason supports the difference of the proportionality factors; however, some discrepancies were already found by Bosman [8], Hejnal [6] and Aagnostopoulos [7]. These effects are smaller than ours, therefore the role of precipitation cannot be neglected.

Determination of the relaxation time. Two different relaxation times were involved in all measurements. The processes were separated into components and analysed with the help of a semi-logarithmic plot in the way shown by Rathenau [9].

Determination of the activation energy. Fig. 3 shows the relaxation times as a function of the reciprocal temperature in a semi-logarithmic plot. The slope of these lines is proportional to the activation energy. The measured points form

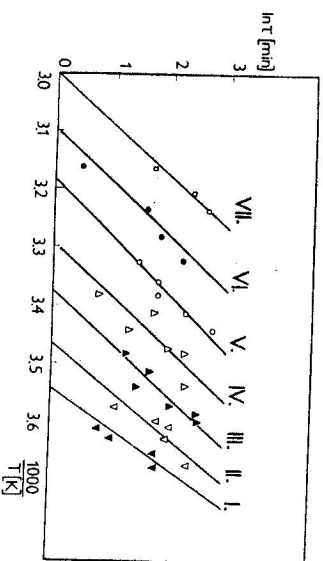


Fig. 3. Determination of the activation energy for interstitial oxygen disaccommodation.

seven lines. The activation energies and pre-exponential factors were determined by the least squares method. The error in the activation energy value is $\pm 10\%$. The values are summarized in Table 3.

We do not think that there are seven physically different relaxations. They can be separated into two groups containing relaxations I—II and III—VII, respectively, because the related processes have similar activation energies.

Processes III—VII will be discussed first. The different relaxation times with similar activation energies are due to the different mobilities of the Bloch-walls and to the superposition of short and long range ordering, as pointed out by Rathenau [9]. The average values of the parameters for relaxations III—VII are: 93.8 kJ/mole and $6.4 \times 10^{-14} \text{ sec}$. These values are in very good agreement with the calculated results and with the dynamical aftereffect measurements. The higher activation energies and shorter relaxation times of processes I—II suggest that they are due to pair reorientation.

Because of the small quantity of solutes, the existence of C—C and O—O pairs is not probable. But as carbon and oxygen have a high chemical affinity, C—O pairs

Table 3

Activation energies and pre-exponential factors of interstitial oxygen disaccommodation							
O (kJ/mole)	1.			2.			
	I.	II.	III.	IV.	V.	VI.	VII.
t_0 (10^6 sec)	111.9	103.9	95.5	99.7	87.1	91.3	95.5
τ_0	1.1	8.5	7.5	3.6	1.7	9.5	5.6
n	19.9	18.0	16.0	16.0	13.0	14.0	14.0

may exist. The formula of Wert [10] was used to determine the binding energy of the pair:

$$\ln(\Delta \cdot T) = C + \frac{E}{RT} \quad (2)$$

where Δ is the amplitude of the aftereffect, T the absolute temperature of the measurement, E the binding energy of the pair, R the universal gas constant, C the constant.

A binding energy of 81.3 ± 16.8 kJ/mole was determined with the help of the least squares method. This value is significantly higher than the usual one of pair binding energies (10–30 kJ/mole), but it can be understood on the basis of the high chemical affinity of the elements (the binding energy of the CO molecule is about 108.9 kJ/mole).

It can be seen that in a material containing carbon it is very difficult to find free oxygen relaxation, and in a material containing oxygen, free carbon relaxation may disappear. Indeed, regarding the parameters of the relaxations in Φ -Fe with less oxygen and in 6-Fe-Al, it can be concluded that the role of C—O pairs must be significant in these processes.

In the Φ -Fe sample, oxidized in an atmosphere containing more oxygen this pair relaxation was not found. Calculating with $Q = 108.1$ kJ/mole and $\tau_0 = 4.3 \times 10^{-18}$ sec this relaxation would appear at 346 ± 30 and 394 ± 30 K at 10 and 1000 Hz, respectively, in the dynamical aftereffect measurements. As the corresponding temperatures for the free carbon and free oxygen relaxations are 339:402 K and 355:417 K, respectively, this process is hidden, due to its small amplitude by the broadened carbon or oxygen relaxation and/or carbon precipitation, which was neglected in the calculations. As the distribution parameters of the fitted curves are: (for definition see Eq. 1a)

$$\begin{aligned} \beta_0 (10 \text{ Hz}) &\sim 1.5 & \beta_1 (10 \text{ Hz}) &\sim 0 \\ \beta_0 (1000 \text{ Hz}) &\sim 0 & \beta_1 (1000 \text{ Hz}) &\sim 2 \end{aligned}$$

it is very probable that the effect of C—O pair-reorientation caused the broadening of the nearer process, which may be oxygen relaxation at 10 Hz and carbon relaxation at 1000 Hz. The 10 Hz—O relaxation and the 1000 Hz—C relaxation had a slightly higher amplitude than the values calculated on the basis of Hejnal's results [6]. This phenomenon may also be due to the above-mentioned effect.

SUMMARY AND CONCLUSIONS

The magnetic aftereffect and disaccommodation measurements carried out on iron and iron-rich Fe—Al alloys containing oxygen proved the interstitial behaviour of oxygen, as supposed by Frank, Engel and Seeger on the basis of theoretical calculations. Regarding the amplitude of the aftereffect, the interaction of oxygen with iron atoms must be similar in nature to that of carbon and nitrogen, in opposition to Levy's calculations [11], who found no interaction with the electron orbits and therefore suggested a smaller amplitude of the aftereffect. Besides the relaxation due to interstitial oxygen, an aftereffect connected with the reorientation of C—O pairs was also found. As the binding energy of the pairs is rather high, the formation of pairs is very significant in these alloys; and it is preferred in the presence of any perturbation (less oxygen in the oxidizing atmosphere, impurities, etc.).

In samples containing oxide-forming elements (Al, Ti) the relaxation due to free interstitial oxygen disappeared, as the interstitial atom formed chemical compounds with the added elements.

This behaviour proves the interstitial nature of the observed oxygen relaxation.

REFERENCES

- [1] Krommüller, H.: *Nachwirkung in Ferromagnetika*. Springer Tracts in Natural Philosophy, Vol. 12. Springer-Verlag, Berlin (Heidelberg) New York 1968.
- [2] Frank, W., Engel, H. J., Seeger, A.: *Z. Metallkde* 58 (1967), 452.
- [3] Stefán, M., Földéáki, M.: "Soft Magnetic Materials 3" Conference Bratislava 13–16. 9. 1977, in press.
- [4] Földéáki, M., Stefán, M.: *INTERMAG 78 Conference*. May 9–12, 1978. Firenze, to be published in IEEE Trans. Mag. Sept. 1978.
- [5] Vojtaník, P., Briandín, J., Gréser, A.: *Elektrotech. Čas.* 29 (1978), 281.
- [6] Hejnal, T.: *Acta phys. pol. A 51* (1977), 379.
- [7] Anagnostopoulos, T.: *Contribution a l'étude des alliages dilués de carbon dans le fer* α . Rapport CEA-R-3904, Grenoble 1971.
- [8] Bosman, A. J.: *Investigation on Magnetic After-Effect Due to Interstitials*. Thesis, Amsterdam 1960.
- [9] Rathenau, G. W.: *J. appl. Phys.* 29 (1958), 239.
- [10] Wert, C. A.: *J. Phys. Chem. Solids* 31 (1970), 1771.
- [11] Levy, P. M.: *J. Phys. Chem. Solids* 26 (1965), 415.

Received December 19th, 1979.