Der Halbleiter-Metall-Übergang in Pyrochloren des Systems $\text{Ln}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ ($\text{Ln} = \text{Pr}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}$)

The Semiconductor-Metal Transition in Pyrochlores of the System $\text{Ln}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ ($\text{Ln} = \text{Pr}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}$)

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Pyrochlores, Anderson Localization, Semiconductor-Metal Transition

In the pyrochlore system $\text{Pr}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ a partial substitution of Pr by Cu is observed for $x \leq 0,375$. With increasing x a gradual semiconductor-metal transition occurs. The change of sign of TCR from negative to positive is observed for $\rho \sim 6 \times 10^{-3} \Omega \text{ cm}$ ($x = 0,2$). The presence of variable range hopping in the insulating regime strongly suggests that the metal-semiconductor transition is of Anderson type. For the pyrochlores of type $\text{Ln}_{1,625}\text{Cu}_{0,375}\text{Ru}_2\text{O}_{7-z}$ with the smaller rare earth ions Sm, Eu, Gd, Dy the metallic conductivity is absent and localization of Anderson type occurs.

Einleitung

Im Rahmen von Untersuchungen über den Halbleiter-Metall-Übergang bei Edelmetall-haltigen Pyrochloren [1–3] interessierte der Einfluß der Substitution von Ln durch Cu auf die Leitungseigenschaften der Pyrochlore $\text{Ln}_2\text{Ru}_2\text{O}_7$ ($\text{Ln} = \text{Seltene Erden}$), die ausnahmslos zu den Halbleitern gehören ([1]; so wie die dort zitierte Literatur). Analoge Untersuchungen am Beispiel der Systeme $\text{Bi}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ [4], $\text{Bi}_{2-x-y}\text{Pb}_y\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ [5] und $\text{Bi}_{2-x}\text{Cu}_x\text{Ru}_{2-y}\text{Ir}_y\text{O}_{7-z}$ [6] hatten bereits ergeben, daß hier die hohe elektrische Leitfähigkeit der Cu-freien Verbindungen erhalten bleibt. Bei halbleitenden Spinellen führt der Cu-Einbau zu einer Erhöhung der elektrischen Leitfähigkeit [7–9]. Im System $\text{Nd}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ soll für $0,1 \leq x \leq 0,375$ metallartige Leitfähigkeit auftreten [10].

Die vorliegende Untersuchung beschäftigt sich mit dem Cu-Einbau in die halbleitenden Pyrochlore $\text{Ln}_2\text{Ru}_2\text{O}_7$: System $\text{Ln}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ ($\text{Ln} = \text{Pr}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}$). In der Reihe $\text{Pr}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ führt die steigende Substitution von Pr durch Cu zu einem kontinuierlichen Halbleiter-Metall-Übergang. Metallische Leitfähigkeit wird für $0,2 \leq x \leq 0,375$ (Phasengrenze) beobachtet. Aus dem Auftreten von drei-

dimensionalem „variable range hopping“ im halbleitenden Bereich kann geschlossen werden, daß der Halbleiter-Metall-Übergang vom Anderson-Typ ist. Mit den kleineren Ln^{3+} -Ionen Sm, Eu, Gd und Dy verschwindet dagegen für $x = 0,375$ die metallartige Leitfähigkeit und es findet Lokalisation vom Anderson-Typ statt.

Experimenteller Teil

Zur Darstellung von Präparaten aus dem System $\text{Ln}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ wurden stöchiometrische Mengen von Pr_4O_7 bzw. Ln_2O_3 ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}$; 99,99%; Rhône Poulenc), CuO (p.A.; Merck) und Ru (99,9%; Heraeus) in einer Achatreischale gründlich verrieben und in Korundtiegeln (Degussit Al 23) an der Luft erhitzt (16 h: 1000 °C; 1 h: 1000 °C; 1 h: 1100 °C). Die Produkte wurden zwischenzeitlich erneut verrieben und der Reaktionsfortgang röntgenographisch (Pulverdiffraktometer von Philips; $\text{CuK}\alpha$ -Strahlung; Au-Standard) und gravimetrisch verfolgt. Die Gewichtsverluste lagen bei < 2%. Die Dichten wurden pyknometrisch (Sperrflüssigkeit: *n*-Oktan) und die elektrischen Widerstände entsprechend [3] sowohl an gepreßten Pulvern als auch an gesinterten Preßlingen bestimmt. Für die gepreßten Pulver lag die Raumerfüllung bei ~92% der Röntgengichte, für die gesinterten Preßlinge bei ~65%. Der spezifische Widerstand wurde ohne Korrektur für die Dichte berechnet.

Löslichkeitsversuche an den einheitlichen Pyrochloren ergab keine Löslichkeit in konzentriertem wäßrigem HCl, HBr, HNO_3 , H_2SO_4 sowie in Königswasser und 30-proz. KOH.

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Ergebnisse

Im System $\text{Pr}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ bilden sich für $0 \leq x \leq 0,375$ einheitliche kubische Pyrochlore. Die beobachteten Auslöschungen erfüllen die Bedingungen der Raumgruppe Fd3m. Die Gitterkonstante (Tab. I) sinkt kontinuierlich mit steigendem x . Präparate mit $x = 0,4$ und $0,5$ sind inhomogen; neben einem Pyrochlor als Hauptprodukt mit praktisch derselben Gitterkonstante wie für $x = 0,375$ ($a = 10,293 \text{ \AA}$) lassen sich mit x wachsende Anteile an RuO_2 nachweisen.

Die Pyrochlore der Zusammensetzung $\text{Ln}_{1,625}\text{Cu}_{0,375}\text{Ru}_2\text{O}_{7-z}$ (Ln = Sm, Eu, Gd, Dy) sind röntgenographisch einheitlich. Die kubischen Verbindungen kristallisieren in der Raumgruppe Fd3m, die Gitterkonstanten (Tab. I) nehmen entsprechend der Ln^{3+} -Größe ab.

Tab. II zeigt die Ergebnisse der Intensitätsberechnungen an Pulverdaten am Beispiel der drei Pyrochlore $\text{Pr}_2\text{Ru}_2\text{O}_7$, $\text{Pr}_{1,625}\text{Cu}_{0,375}\text{Ru}_2\text{O}_{7-z}$ und $\text{Dy}_{1,625}\text{Cu}_{0,375}\text{Ru}_2\text{O}_{7-z}$ für die Raumgruppe Fd3m (allgemeine Formel $\text{A}_2\text{B}_2\text{O}_6\text{O}'$) mit A in 16d, B in 16c, O in 48f und O' in 8b und den isotropen Temperaturfaktoren $B_{\text{Pr}} = B_{\text{Cu}} = 0$; $B_{\text{O}} = B_{\text{O}'} = 0,5$ (Pr; $x = 0$); $1,0$ (Pr; $x = 0,375$); $1,5 \text{ \AA}^2$ (Dy; $x = 0,375$). Der Zuverlässigkeitsfaktor $R' (\sum |I_o - I_c| / \sum I_c)$ beträgt jeweils etwa 4%. Der Sauerstoffparameter x_0 von O (48f) liegt mit etwa $0,345$ (Pr; $x = 0$); $0,342$ (Pr; $x = 0,375$); $0,324$ (Dy; $x = 0,375$) über dem Wert für eine ideale Pyrochlorstruktur mit $x_0 = 0,3125$ [11]. Im System $\text{Pr}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ führt der Ersatz von Pr durch Cu zu einer Verkürzung der Ru–O-Abstände von $2,08$ ($x = 0$) auf $2,05 \text{ \AA}$ ($x = 0,375$). Für $\text{Dy}_{1,625}\text{Cu}_{0,375}\text{Ru}_2\text{O}_{7-z}$ liegt der entsprechende Wert bei $1,95 \text{ \AA}$.

Tab. I. Gitterkonstanten ($\text{\AA}$), Dichte ($\text{g} \cdot \text{cm}^{-3}$), spezifischer Widerstand ϱ und Temperaturkoeffizient des Widerstands (TCR) für $\text{Pr}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ und $\text{Ln}_{1,625}\text{Cu}_{0,375}\text{Ru}_2\text{O}_{7-z}$.

x/Ln	a^a	Dichte ber.	gef. ^b	$\varrho (\Omega \text{ cm})^c$ 77 K	300 K	TCR (ppm/K)
$\text{Pr}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$						
0	10,373	7,092	6,83	$1,0 \times 10^2$ ($1,3 \times 10^2$)	$6,5 \times 10^{-1}$ ($6,8 \times 10^{-1}$)	$-6,92 \times 10^5$
0,05	10,362	7,069	6,72	$2,1 \times 10^0$ ($2,3 \times 10^0$)	$4,9 \times 10^{-2}$ ($5,1 \times 10^{-2}$)	$-1,89 \times 10^5$
0,1	10,350	7,047	6,79	$1,0 \times 10^{-1}$ ($1,2 \times 10^{-1}$)	$1,3 \times 10^{-2}$ ($2,1 \times 10^{-2}$)	-30280
0,15	10,339	7,023	6,84	$9,2 \times 10^{-3}$ ($9,2 \times 10^{-3}$)	$7,8 \times 10^{-3}$ ($8,4 \times 10^{-3}$)	-810
0,2	10,328	6,999	–	$5,3 \times 10^{-3}$ ($5,5 \times 10^{-3}$)	$6,6 \times 10^{-3}$ ($7,1 \times 10^{-3}$)	$+890$
0,25	10,317	6,974	6,79	$3,5 \times 10^{-3}$ –	$5,0 \times 10^{-3}$ ($5,2 \times 10^{-3}$)	$+1360$
0,35	10,298	6,919	–	$1,8 \times 10^{-3}$ –	$2,9 \times 10^{-3}$ ($3,4 \times 10^{-3}$)	$+1720$
0,375	10,292	6,907	6,89	$1,0 \times 10^{-3}$ ($1,1 \times 10^{-3}$)	$1,8 \times 10^{-3}$ ($1,9 \times 10^{-3}$)	$+2010$
$\text{Ln}_{1,625}\text{Cu}_{0,375}\text{Ru}_2\text{O}_{7-z}$						
Sm	10,243	7,197	–	$2,1 \times 10^{-2}$ ($2,5 \times 10^{-2}$)	$1,0 \times 10^{-2}$ ($1,2 \times 10^{-2}$)	-4980
Eu	10,225	7,267	–	$5,0 \times 10^{-2}$ –	$1,7 \times 10^{-2}$ –	–
Gd	10,199	7,431	7,37	$8,4 \times 10^{-2}$ –	$1,9 \times 10^{-2}$ –	–
Dy	10,157	7,632	–	$5,3 \times 10^0$ ($5,7 \times 10^0$)	$1,4 \times 10^{-1}$ ($1,5 \times 10^{-1}$)	$-1,67 \times 10^5$

^a $\pm 0,003$; ^b $\pm 0,05$; ^c für alle Zusammensetzungen sind die Werte für gepreßte Pulver angegeben, die Werte für gesinterte Preßlinge befinden sich in Klammern.

	$\text{Pr}_2\text{Ru}_2\text{O}_7$	$\text{Pr}_{1,625}\text{Cu}_{0,375}\text{Ru}_2\text{O}_{7-z}$	$\text{Dy}_{1,625}\text{Cu}_{0,375}\text{Ru}_2\text{O}_{7-z}$
a	10,373	10,292	10,157
x_0	0,345	0,342	0,324
R'	3,60	3,78	3,28
A–A	3,67	3,64	3,59
A–B	3,67	3,64	3,59
B–B	3,67	3,64	3,59
A–O	2,44	2,44	2,53
A–O'	2,25	2,23	2,20
B–O	2,08	2,05	1,95

Tab. II. Gitterkonstanten a ($\text{\AA}$), x_0 von O in 48f; R' (%) und interatomare Abstände ($\text{\AA}$).

Der spezifische Widerstand von $\text{Pr}_2\text{Ru}_2\text{O}_7$ (Tab. I) fällt in die gleiche Größenordnung wie für die anderen halbleitenden Pyrochlore $\text{Ln}_2\text{Ru}_2\text{O}_7$ [1, 10, 12]. Die Übereinstimmung zwischen den an gepreßten Pulvern und gesinterten Preßlingen erhaltenen Werte ist, ebenso wie für alle weiteren untersuchten Pyrochlore (Tab. I), sehr gut. Wenn auch allein von Messungen an fehlerfreien Einkristallen exakte Aussagen über den wahren Widerstand zu erwarten sind, ermöglicht die gute Übereinstimmung der hier an keramischen Proben erhaltenen Meßwerte die Änderung der elektrischen Leitfähigkeit zuverlässig wiederzugeben.

Aus der Temperaturabhängigkeit des spezifischen Widerstands im System $\text{Pr}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ ($x \leq 0,375$) in Abb. 1 sowie Tab. I geht hervor, daß für $0,2 \leq x \leq 0,375$ metallartige Leitfähigkeit mit einem positiven Temperaturkoeffizienten TCR ($= (1/\varrho) (d\varrho/dT)$) vorliegt. Mit sinkendem x geht TCR zurück. Für $x \leq 0,15$ ist TCR negativ und wächst mit abnehmendem x [13].

Den Übergang von metallischen zu halbleitenden Eigenschaften mit abnehmendem x geben die IR-Spektren des Systems $\text{Pr}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ ebenfalls wieder (Abb. 2). Verbindungen mit $x \geq 0,1$ zeigen eine kontinuierliche Absorption, die für eine hohe

Abb. 1. Temperaturabhängigkeit des spezifischen Widerstands ($\log \varrho$) für das System $\text{Pr}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ ($x \leq 0,375$).

Abb. 2. IR-Spektren aus dem System $\text{Pr}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$; zur besseren Übersicht ist der Ordinatenmaßstab gegeneinander verschoben (* Polyethylenbande).

Konzentration an freien Ladungsträgern charakteristisch ist, dagegen entwickelt sich mit $x < 0,05$ das typische, einer geringen Konzentration an freien Ladungsträgern entsprechende Spektrum von Verbindungen mit Pyrochlorstruktur. Entsprechend den Beobachtungen in anderen Systemen (vgl. [3] sowie die dort angeführte Literatur) verschwinden die Banden in den IR-Spektren für $\varrho \sim 10^{-1} \Omega \text{ cm}$, einem Wert, der etwa zwei Größenordnungen über demjenigen Widerstandswert liegt, für den TCR sein Vorzeichen ändert.

Um Auskünfte über den Transportmechanismus der Elektronen zu erhalten, wurde in Abb. 3 $\ln \sigma$ als Funktion von $1/T$ aufgetragen. Die Leitfähigkeit der im halbleitenden Gebiet des Halbleiter-Metall-Übergangs befindlichen Pyrochlore zeigen das charakteristische thermisch aktivierte Verhalten. Die Aktivierungsenergie bleibt jedoch temperaturabhängig. Dieses Verhalten deutet auf einen Transport durch

Abb. 3. $\ln \sigma$ vs $1/T$ für das System $\text{Pr}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ ($0 \leq x \leq 0,15$).

dreidimensionales (3D) „variable range hopping“ hin [11]. In Abb. 4 wurde daher $\ln \sigma$ für $0 \leq x \leq 0,15$ als Funktion von $T^{-1/4}$ aufgetragen. Für $0,05 \leq x \leq 0,15$ ergibt sich eine gut definierte $T^{-1/4}$ -Abhängigkeit.

Abb. 4. $\ln \sigma$ vs $1/T^{1/4}$ für das System $\text{Pr}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ ($0 \leq x \leq 0,15$).

Im Gegensatz zu den metallartig leitenden Cu-reichen Pyrochloren des Systems $\text{Pr}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ ($0,2 \leq x \leq 0,375$) gehören die Cu-reichen Pyrochlore $\text{Ln}_{1,625}\text{Cu}_{0,375}\text{Ru}_2\text{O}_{7-z}$ ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}$) bereits zu den Halbleitern; der negative TCR steigt mit sinkender Ln^{3+} -Größe an (Tab. I). Am Beispiel von $\text{Dy}_{1,625}\text{Cu}_{0,375}\text{Ru}_2\text{O}_{7-z}$ ist in Abb. 5 $\ln \sigma$ als Funktion von $1/T$ (5a) bzw. $1/T^{1/4}$ (5b) aufgetragen. Aus der Gültigkeit der $T^{-1/4}$ -Beziehung geht hervor, daß Lokalisation vom Anderson-Typ vorliegt.

Abb. 5a. $\ln \sigma$ vs $1/T$ für $\text{Dy}_{1,625}\text{Cu}_{0,375}\text{Ru}_2\text{O}_{7-z}$.

Abb. 5b. $\ln \sigma$ vs $1/T^{1/4}$ für $\text{Dy}_{1,625}\text{Cu}_{0,375}\text{Ru}_2\text{O}_{7-z}$.

Diskussion

Im System $\text{Pr}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ läßt sich Pr partiell durch Cu ersetzen; die Phasengrenze liegt bei $x \sim 0,375$. Während $\text{Pr}_2\text{Ru}_2\text{O}_7$ zu den Halbleitern gehört, zeigen die Cu-reicheren Glieder ($0,2 \leq x \leq 0,375$) metallartige Leitfähigkeit. Mit steigendem x findet

ein kontinuierlicher Halbleiter-Metall-Übergang statt, strukturelle Diskontinuitäten sind nicht zu erkennen. Der Vorzeichenwechsel von TCR erfolgt für $\rho \sim 6 \times 10^{-3} \Omega \text{ cm}$, einem Bereich, der der bekannten minimalen metallischen Leitfähigkeit von Mott entspricht; in anderen Oxidsystemen findet der Vorzeichenwechsel von TCR im gleichen Gebiet statt ([15] sowie die dort zitierte Literatur). Der Metall-Halbleiter-Übergang ist für die Reihe $\text{Pr}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ vom Anderson-Typ. Eine analoge Beobachtung wurde bei den Pyrochloren des Systems $\text{Bi}_{2-x}\text{Pb}_x\text{Pt}_{2-x}\text{Ru}_x\text{O}_{7-z}$ gemacht [3]. Unter den Perowskiten liefern die Systeme $\text{Ln}_{1-x}\text{Ca}_x\text{MnO}_3$ ($\text{Ln} = \text{La}, \text{Nd}$) weitere Beispiele [16].

Die elektrische Leitfähigkeit Ru-haltiger Pyrochlore $\text{A}_2\text{Ru}_2\text{O}_{7-z}$ wurde wiederholt diskutiert [17–20]. Nach neueren Untersuchungen über die Bandstruktur von $\text{Y}_2\text{Ru}_2\text{O}_7$ [21] liegen die 5s- und 5p-Bänder des Y zwischen 5 und 10 eV oberhalb der Fermi-Energie (E_F) und die Zustandsdichte bei E_F ist sehr klein. $\text{Y}_2\text{Ru}_2\text{O}_7$ besitzt daher bei E_F ein schmales t_{2g} -Band und ist ein Mott-Isolator. Von den 4f-Elektronen der kleineren Seltenen Erden (z.B. Eu^{3+} , Gd^{3+}) ist ebenfalls bekannt, daß sie lokalisiert sind und die elektrische Leitfähigkeit in geringerem Maße beeinflussen als die 4f-Elektronen der größeren Seltenen Erden (z.B. La^{3+}) mit stärker ausge-

dehnten Orbitalen, welche mit benachbarten Zuständen hybridisieren können [22]. Die hier bei den Verbindungen $\text{Ln}_{1,625}\text{Cu}_{0,375}\text{Ru}_2\text{O}_{7-z}$ beobachtete Änderung der elektrischen Leitfähigkeit von halbleitend ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}$) nach metallisch ($\text{Ln} = \text{Pr}$) deutet ebenfalls auf eine Änderung der Bandstruktur durch das stärker ausgedehnte 4f-Band von Pr hin. Der Halbleiter-Metall-Übergang innerhalb der Reihe $\text{Pr}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ wird durch die mit steigendem x beobachtete Kontraktion der Metall-Sauerstoff-Abstände (Tab. II) begünstigt. Für eine Beteiligung von Cu-Bändern an der Bandleitfähigkeit im metallischen Bereich von $0,2 \leq x \leq 0,375$ spricht, daß der minimale Cu-Gehalt von $x \sim 0,2$ nahe dem Erwartungswert von Standard-Perkolationsmodellen liegt [23, 24].

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- [1] A. Ehmann und S. Kemmler-Sack, *Mat. Res. Bull.* **20**, 437 (1985).
- [2] E. Beck und S. Kemmler-Sack, *J. Less-Common Met.* **136**, 257 (1987).
- [3] G. Mayer-von Kürthy, W. Wischert, R. Kiemel, S. Kemmler-Sack, R. Groß und R. P. Hübener, *J. Solid State Chem.* **79**, 34 (1989).
- [4] M. Schuler und S. Kemmler-Sack, *J. Less-Common Met.* **102**, 105 (1984).
- [5] E. Beck und S. Kemmler-Sack, *J. Less-Common Met.* **113**, 65 (1985).
- [6] E. Beck und S. Kemmler-Sack, *Mat. Res. Bull.* **21**, 307 (1986).
- [7] B. Krutzsch und S. Kemmler-Sack, *Mat. Res. Bull.* **19**, 1659 (1984).
- [8] B. Krutzsch und S. Kemmler-Sack, *J. Less-Common Met.* **124**, 155 (1986).
- [9] B. Krutzsch und S. Kemmler-Sack, *J. Less-Common Met.* **132**, 37 (1987).
- [10] A. Haouzi, J. Muller und J. C. Joubert, *Mat. Res. Bull.* **21**, 1489 (1986).
- [11] M. A. Subramanian, G. Aravamudan und G. V. Subba Rao, *Progr. Solid State Chem.* **15**, 55 (1983).
- [12] A. W. Sleight und R. J. Bouchard, *NBS Special Publ.* 364, *Solid State Chem.*, Proc. 5th Mat. Res. Symposium, 227 (1972).
- [13] Im System $\text{Nd}_{2-x}\text{Cu}_x\text{Ru}_2\text{O}_{7-z}$ wird für $0,1 \leq x \leq 0,375$ metallartige Leitfähigkeit beobachtet [10]. Die Proben mit 0,1 und 0,2 wurden unter Zusatz von 5% CuO gegläht. Nach eigenen Untersuchungen findet dabei jedoch eine chemische Reaktion unter Bildung Cu-reicher Pyrochlore statt, so daß die beobachtete Leitfähigkeit verfälscht sein kann.
- [14] N. F. Mott, *The Metallic and Nonmetallic States of Matter* (P. P. Edwards and C. N. R. Rao, Editors), p. 1, Taylor and Francis, London and Philadelphia (1985).
- [15] R. Vijayaraghavan, R. A. Mohan Ram, P. Ganguly und C. N. R. Rao, *Mat. Res. Bull.* **23**, 719 (1988).
- [16] H. Taguchi, M. Nagao und M. Shimada, *J. Solid State Chem.* **76**, 284 (1988).
- [17] J. M. Longo, P. M. Raccach und J. B. Goodenough, *Mat. Res. Bull.* **4**, 91 (1969).
- [18] P. A. Cox, R. G. Egdell, J. B. Goodenough, A. Hamnett und C. C. Naish, *J. Phys.* **C 16**, 6221 (1983).
- [19] R. G. Egdell, J. B. Goodenough, A. Hamnett und C. C. Naish, *J. Chem. Soc. Faraday Trans.* **79**, 893 (1983).
- [20] P. A. Cox, J. B. Goodenough, P. J. Tavener, D. Telles und R. G. Egdell, *J. Solid State Chem.* **62**, 360 (1986).
- [21] W. Y. Hsu, R. V. Kasowski, T. Miller und T.-C. Chiang, *Appl. Phys. Lett.* **52**, 792 (1988).
- [22] N. Ikeda, K. Kohn, E. V. Sampathkumaran und P. Vijayaraghavan, *Solid State Comm.* **68**, 51 (1988).
- [23] H. Scher und R. Zallen, *J. Chem. Phys.* **53**, 3759 (1970).
- [24] I. Balberg und N. Binenbaum, *Phys. Rev.* **B35**, 8749 (1987).

Graphite Compounds with Chlorine Trifluoride

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Chlorine Trifluoride, Graphite Compounds, Graphite Fluoride,
Graphite Intercalation Compounds

Graphite intercalation compounds of the acceptor type are formed with ClF_3 only at low temperatures near 0 °C. Different compounds are obtained in the absence or in the presence of HF. Thermal decomposition near room temperature or preparation at 20–50 °C lead to green or yellow-green graphite compounds of the covalent type, which differ, however, in their X-ray diffraction patterns and IR spectra from the graphite fluorides prepared at high temperatures.

Introduction

Many element fluorides and chlorides are intercalated in graphite [1]. Acceptor compounds are formed in the reaction, that means that electrons are transferred from the carbon layers of graphite – also called graphene layers [2] – to the intercalated substance. Either discrete anions are intercalated or the electrons are more or less delocalized in the intercalated layers as *e.g.* in FeCl_3 -graphite.

Stage 1 acceptor compounds in which every interlayer space is filled with intercalate frequently have the general formula $\text{C}_x^+ \text{EX}_n^- \cdot m \text{Y}$ with Y being either free element halide or solvent molecules; x has usually a value between 24 and 27. Such compounds present a steel-blue, metallic appearance due to the position of the Drude plasma edge. Higher stage compounds with a smaller proportion of filled interlayers between the graphene layers are shiny black.

Often, in the case of very reactive fluorides, the carbon layers will be more or less strongly fluorinated with formation of covalent C–F bonds. Surface fluorination has been observed even with SbF_5 after relatively long reaction times [3].

The intercalation of ClF_3 in graphite has been described in the literature but the reports disagree on the appearance and composition of the reaction products. Selig *et al.* [4] described a compound of the approximate formula $\text{C}_{31}\text{FCl}_8$ which did not differ markedly in its appearance from the original graphite. ClF was formed as a by-product in the reac-

tion. A green, hydrophobic product of the composition $\text{C}_{14}^+ \text{H}_2 \text{F}_3^- \text{ClF}_2^+ \text{HF}_2^-$ ($= \text{C}_{14} \text{ClF}_7 \text{H}_3$) was obtained from a ClF_3 solution in anhydrous hydrogen fluoride at 22 °C [5]. Other authors found a composition $\text{C}_{14.4} \text{ClF}_{6.3} \cdot 1.5 \text{HF}$ ($= \text{C}_{14.4} \text{ClF}_{7.8} \text{H}_{1.5}$) [6]. Pale-yellow, transparent platelets with the composition $\text{C}_4 \text{F} \cdot 0.46 \text{ClF}_3$ ($= \text{C}_{8.7} \text{ClF}_{5.2}$) were formed after 15–20 days at 0 °C with a solution of CsF in ClF_3 [7, 8]. The appearance and a very low electrical conductivity are indications that this compound is not an acceptor intercalation compound but a covalent compound related to graphite fluoride, $(\text{CF}_x)_n$. It was concluded from the infrared and ^{19}F NMR spectra that mobile ClF_3 molecules are intercalated between fluorinated carbon layers, no C–Cl bonds could be detected [8, 9]. In contrast, considerable electrical conductivity at 293–346 K was found by Nikonorov *et al.* [10]. Very recently it has been reported that no carbon fluorination occurs in the absence of HF [11]. With ClF_3 , HF and F_2 black $\text{CCl}_{0.06}\text{F}_{0.52}$ ($= \text{C}_{16.6} \text{ClF}_{8.7}$) and green $\text{CCl}_{0.05}\text{F}_{0.65}$ ($= \text{C}_{20} \text{ClF}_{13}$) were obtained. Both compounds produced quite similar X-ray diffraction patterns.

With BrF_3 , similar to ClF_3 , the observations are also contradictory: a green compound has been described [12] whilst other authors [13] claimed that the appearance of the reaction product, $\text{C}_{8.9} \text{BrF}_3$ was similar to that of graphite, apart from an increase in volume. Also compositions between $\text{C}_{18} \text{BrF}_{12}$ [14] and $\text{C}_{16.1} \text{BrF}_{9.3}$ [15] have been found for the reaction product of graphite with liquid BrF_3 , indicating heavy carbon fluorination. According to Selig *et al.* the reaction product of graphite with BrF_3 of the approximate composition $\text{C}_{24} \text{BrF}_{13}$ is very similar to the dark green material obtained with BrF_5 [4].

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These discrepancies in the descriptions of the reaction products led us to study the reaction of graphite with ClF_3 in more detail. The green color seemed to indicate an electronic structure different from that in the usual acceptor compounds. We succeeded in preparing blue intercalation compounds at low temperature.

Experimental

Natural graphites of better than 99.5% purity were used: S 40 flakes with a particle diameter of 0.2–1 mm, and AF powder (1–10 μm) were from Kropfmühl, Bavaria; Madagascar flakes (*ca.* 1 mm) were also used. Authentic white graphite fluoride $(\text{CF}_{1.12})_n$ was provided by the Ozark-Mahoning Co. (USA).

ClF_3 (98%) from Matheson Comp., and HF from Linde were used. The gases were first condensed at -60°C into a Monel cylinder until the level of the liquid reached an electrode introduced through a screwed-in PTFE plug, producing an electrical contact between the electrode and the cylinder. Usually, 6 ml were thus condensed. The liquids, first HF, then ClF_3 were distilled into a second Monel cylinder containing between 1 and 5 g of the graphite. The temperature of this cylinder was thermostated ($\pm 0.5^\circ\text{C}$) between 0 and 50°C . After reaction times between 1 and 5 days, the excess reagent was blown out in an N_2 stream (for reaction temperatures of 20°C or higher) and passed over crushed silicon for destruction of the ClF_3 , or it was vacuum-distilled into a cold trap (-75°C). The samples were finally dried in an N_2 stream. The apparatus, consisting of Monel and copper, was checked for leaks before each experiment. In a dry glove-box the samples were transferred to Schlenk tubes for further handling.

For chemical analysis, parts of the samples were treated in a Parr bomb with a fused $\text{Na}_2\text{O}_2/\text{NaOH}$ mixture (addition of a little diethyleneglycol-diethylether facilitated ignition on heating). Chloride was determined by potentiometric titration with 0.001 M AgNO_3 , and fluoride by titration with 0.033 M $\text{La}(\text{NO}_3)_3$ at pH 5.5 with use of a fluoride-sensitive electrode (Orion). For Debye-Scherrer X-ray analysis the samples were filled into capillaries of Lindemann glass. Infrared spectra were taken by the KBr pellet technique.

Discussion

Table I presents the analytical data for a selection of typical preparations. At first sight, one sees that the color of most of the samples is the lighter, going from black to dark blue to green, and to yellowish-green, the higher the temperature of preparation was. An exception was sample no. 2 prepared at 12°C which had the lightest color and a relatively high fluorine content. However, this sample was exfoliated indicating that there might have been a thermal excursion due to an exothermic reaction. Sample no. 4 which was also exfoliated had a similarly high fluorine content. The F/C ratio in the exfoliated samples was slightly above 1.00. On microscopic inspection such samples appeared inhomogeneous in color.

The green samples did not have a metallic luster and did quite obviously not belong to the group of metallic acceptor compounds. They were practically electrical insulators. The samples were hydrophobic, and most of them were stable in air or in contact with water. Fluoride and chloride could be detected in water only with samples prepared below 10°C . The glass vessels showed traces of HF etching only after several days.

Sample no.	Starting material	Reaction temp.	Reaction time	Color	Cl [%]	F [%]	Approx. formula
17	S 40	0°C	3 d	blue-black	9.8	28.9	$\text{C}_{10}\text{ClF}_{5.5}$
10	Mad.	0°C	3 d	dark blue, shiny	12.2 ^a	37.3 ^a	$\text{C}_{12}\text{ClF}_{5.7}$ ^a
11	Mad.	5°C	3 d	blue-black	16.1	33.8	$\text{C}_9\text{ClF}_{3.9}$
12	Mad.	5°C	3 d ^b	grey-black, shiny	10.6	44.4	$\text{C}_{12}\text{ClF}_{7.8}$
9	AF	20°C	2 d	light blue, dull	10.7	31.9	$\text{C}_{16}\text{ClF}_{5.6}$
4	S 40	20°C	5 d	blue-green, exfoliated	11.2	54.6	$\text{C}_9\text{ClF}_{9.1}$
6	AF	30°C	1 d	olive green	14.5	34.5	$\text{C}_{10.4}\text{ClF}_{4.5}$
5	AF	50°C	1 d	light green	12.6	45.3	$\text{C}_{9.8}\text{ClF}_{6.7}$
2	S 40	12°C	1 d	yellow-green, exfoliated	12.1	54.3	$\text{C}_{8.2}\text{ClF}_{8.4}$

Table I. Preparation conditions and chemical composition of the reaction products of graphite with HF + ClF_3 .

^a After spontaneous decomposition, see text; ^b reaction with ClF_3 only, no HF added.

The shiny, dark blue compound no. 10, however, began to decompose exothermally shortly after transfer to the Schlenk tube. Cl_2 or ClF was evolved and the glass was heavily etched, yet the flakes were barely exfoliated. The color of the material changed to blue-green within 10 hours. The analytical data, the diffractogram and the infrared spectrum could only be obtained from the decomposed sample.

The ratio of fluorine to chlorine was in most cases near to 5 ± 0.5 , and higher in the samples which showed the lightest coloring. Nazarov *et al.* [8] had observed in their preparation a similar ratio of 5.17, although their pale-yellow material was richer in $(\text{Cl} + \text{F})$ than our compounds.

In a second set of experiments the graphite was treated with the vapor over a 1:1 (by volume) mixture of ClF_3 and HF . The liquid mixture and the graphite were maintained at the same, constant temperature. As shown in Table II, in this case the ratio F/C increased drastically with the temperature (the vapor pressure of pure ClF_3 increases from 0 °C

to 12 °C only from $6 \cdot 10^4$ Pa to $9.7 \cdot 10^4$ Pa); there was also a marked decrease in the F/Cl ratio. The samples no. 13–15 contained free graphite and remained black. Only the freshly prepared sample no. 16 showed a distinct blue color, which changed to black after several days storage at –20 °C. Analyses and X-ray patterns were determined immediately after preparation in this case.

It has been claimed that carbon fluorination occurs only in the presence of HF [8, 11]. We found, however, that our sample no. 12 which was prepared without HF addition had a much higher $\text{F}:\text{Cl}$ ratio than the material prepared at the same temperature with HF present. This sample differed from the other samples not only in appearance but also in its X-ray diffraction pattern. In this case a neat $(00l)$ series with $l = 1$ to 4 was found whilst the other samples gave relatively broad reflections as listed in Table III. The (100) and (110) reflections were always present in addition, indicating no significant increase in the a -axis relative to graphite. With most

Sample no.	Starting material	Reaction temp.	Reaction time	Cl [%]	F [%]	Composition
13	AF	0 °C	4 d	0.89	7.7	$\text{C}_{304}\text{ClF}_{16}$
14	S 40	5 °C	10 d	1.40	9.4	$\text{C}_{189}\text{ClF}_{12.6}$
15	S 40	8 °C	10 d	2.46	11.9	$\text{C}_{103}\text{ClF}_{9.0}$
16	S 40	12 °C	10 d	7.66	19.6	$\text{C}_{26}\text{ClF}_{4.8}$

Table II. Preparation conditions and analyses after reaction with gaseous $\text{ClF}_3 + \text{HF}$.

Table III. X-ray diffraction patterns.

Sample no.	Observed reflections* [pm]					
12	Four $(00l)$ reflections for $d_l = 7.00$ pm					
16	790 s		385 vs	330 vs	247 s	182 w
17	740 s	550 m	420 m	345 vs	245 s	171 w
10	745 vs	522 s	404 vw	290 w		
11		545 s		325 vs	205 w	162 w
9		595 vs		300 w		
4	760 vs		534 s	375 m	300 w	
6		644 vs				
5	760 s	635 m	535 mw			
2	745 vs		528 s	382 m	316 vw	
$\text{C}_{14}\text{ClF}_7\text{H}_3$ [5]		664 vs		421 vw		179 m
$\text{C}_{8.7}\text{ClF}_{5.2}$ [8]	750 vs		554 s		328 w	226 w
$\text{CF}_{1.12}$		577 s			286 m	191 w
C_2F [23]	≈ 815 vs			405 w	270 vw	

* (100) and (110) of the graphene layers were always observed (≈ 213 and ≈ 123 pm). In most samples also weak reflections fitting the pattern for $\text{NiSiF}_6 \cdot 6 \text{H}_2\text{O}$ were observed.

samples there were faint sharp lines corresponding to the most intense lines of $\text{NiSiF}_6 \cdot 6\text{H}_2\text{O}$ (ASTM index 8–8). One sample showed these lines in higher intensity allowing identification. Other transition metal hexafluorosilicates give similar diffraction patterns. Presumably, the ClF_3 was contaminated with SiF_4 . The samples had been exposed to moist air during filling of the capillaries; very likely this is the source of the water of hydration. On thermal decomposition of the samples small concentrations of SiF_4 could be detected in the gaseous products together with ClF_3 and ClF .

The layer spacing of 700 pm of sample no. 12 excludes double-layers of chlorine atoms in the intercalated layers as in AlCl_3 -graphite ($d_1 = 954$ pm). The value of 700 pm would fit well, however, for a single layer of Cl atoms, as in AuCl_3 -graphite ($d_1 = 680$ pm [16]), implying that the T-shaped ClF_3 molecules are intercalated in a flat position.

For graphite with intercalated hydrogen fluoride (oxidation with F_2) spacings larger than 750 pm or smaller than 670 pm have been reported [17].

The d values for the X-ray reflections are summarized in Table III. For comparison, the diffraction patterns described in the literature for the reaction products of graphite with ClF_3 , are included in the table as well as those of $\text{CF}_{1.12}$ and C_2F . In the case of carbon monofluoride, CF_{1-x} , the layer spacing increases with decreasing F content [18].

There were only a few, relatively broad diffraction lines observed with the samples prepared in the presence of HF. Some of these can be indexed as second order reflections but there was no extended (00 l) series as is usually observed with acceptor compounds. In the case of sample no. 16, the lines at 790, 385, 246 and 182 pm could be tentatively indexed as a (00 l) series with $d_1 \approx 740$ –770 pm. The strong peaks at 750 ± 10 and 530–550 pm seem to be both (00 l) reflections as can be deduced from the analogy of the spot patterns of the lines in the case of large-flake preparations which show preferred orientation in the X-ray capillaries. There is no simple relationship between these spacings, they must arise from different phases. A clear interpretation of the diffraction patterns is not possible. Spacings of ca. 750 and 670–640 pm have also been observed for graphite chemically or electrochemically oxidized in anhydrous HF [17]. The general formula $\text{C}_x^+\text{F}^-(\text{HF})_y$ suggests that these are acceptor-type compounds, however.

Infrared spectroscopy was used in attempts to elucidate the nature of the intercalated species. Fig. 1 shows a few typical spectra. Many of our spectra looked generally similar, with variations in the details. The spectrum of the decomposed compound no. 10 was similar to the spectra shown by Nazarov *et al.* [7, 8] for $\text{C}_{8.7}\text{ClF}_{5.2}$, but it is much better resolved. However, in their sample the peak near 1100 cm^{-1} was much more intense than that at ca. 1220 cm^{-1} . There is general agreement that the absorptions at 1050 – 1100 cm^{-1} and ca. 1220 cm^{-1} arise from C–F bonds. The latter peak coincides with the main absorption of $(\text{CF}_{1.12})_n$. Poly(tetrafluoroethylene) produces two bands at 1155 and 1225 cm^{-1} .

The samples no. 4 and 5 showed the absorption peaks of HF_2^- , but it cannot be ruled out that this

Fig. 1. IR absorption spectra of characteristic reaction products of graphite with ClF_3 (see Table I). For comparison the spectra of KHF_2 and of $\text{CF}_{1.12}$ are also shown.

species was formed in the KBr pellet by hydrolysis (KBr contains always some moisture).

The peaks near 650 and 740 cm^{-1} have been ascribed to ClF_2^+ [5]. Apart from the implausibility of the existence of such a species in the compounds, it follows from Fig. 1 that both peaks vary in their relative intensity, and hence cannot arise from the same species. The presence of ClF_4^- , which has been assumed by Nazarov *et al.* [7], can also be ruled out since this ion absorbs strongly in the range 400–600 cm^{-1} [19]. These authors ascribed the strong peak at 750 cm^{-1} to ClF_3 . However, this compound produces weak absorptions at 760 and 742 cm^{-1} , and a strong peak at 702 cm^{-1} [20]. Therefore, taking into account the shift to lower wave numbers by 30–50 cm^{-1} in the adsorbed state, one could associate the strong peak at 645 cm^{-1} with ν_4 of ClF_3 . The peak at 320 cm^{-1} would fit with ν_3 of ClF_3 (328 cm^{-1}). However, ν_5 at 442 cm^{-1} is also intense for free ClF_3 , and there are only weak peaks in our spectra near this wave number.

The sharp peak at 482 cm^{-1} with sample no. 4 could arise from SiF_6^{2-} , with the second, somewhat larger band at 741 cm^{-1} [21] contributing to the relatively high peak near 745 cm^{-1} . Contributions by ClF to this band (758 and 786 cm^{-1} [22]) appear possible, but this could be only a minor constituent. The peak at 745 cm^{-1} may also be caused by C–Cl bonds. The relatively weak absorption at 1585 cm^{-1} which also appears in some of our spectra has been attributed to C=C double bonds [7].

No IR spectra could be measured with the samples no. 11–17 because of their strong absorption.

Conclusions

True intercalation compounds of the acceptor type can be obtained with ClF_3 only at low temperatures, near 0 °C. In the absence of hydrogen fluoride a stage 1 compound with an interlayer spacing of 700 pm was found. However, in contrast to literature reports, heavy carbon fluorination occurred as well. Also in the presence of HF, metallic, blue first-stage compounds were formed, which are very unstable and decompose at room temperature to covalent graphite compounds. The intercalated species could not be determined but the presence of ClF_3 can be inferred from the instability and from the fact that some ClF_3 was evolved on heating. Graphite hydrofluorides are stable at room temperature.

During decomposition, or on preparation at slightly higher temperatures, the color of the preparations evolves from metallic blue to dull blue, green, and finally yellow. Possibly the green color results from the encapsulation of small blue particles in a yellow matrix. The hydrophobic, electrically insulating materials appear to be covalent graphite compounds. Their X-ray diffraction patterns are similar to those observed with other graphite-fluorine compounds. The infrared spectra show however, that the samples differ considerably from graphite monofluoride, $(\text{CF})_n$. Substoichiometric covalent $(\text{CF}_{1-x})_n$ compounds, and also $(\text{C}_2\text{F})_4$, are grey to black and show larger interlayer spacings.

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- [1] L. B. Ebert, Ann. Rev. Mater. Sci. **6**, 181 (1976); H. Selig and L. B. Ebert, in Adv. Inorg. Chem. and Radiochem. (ed. H. J. Emeléus and A. G. Sharpe), Vol. 23, p. 281, Academic Press, New York (1980); W. C. Forsman, T. Dziemianowicz, K. Leong, and D. Carl, Synth. Met. **5**, 77 (1983).
- [2] H. P. Boehm, R. Setton, and E. Stumpp, Synth. Met. **11**, 363 (1985); Carbon **24**, 241 (1986).
- [3] L. Streifinger, H. P. Boehm, R. Schlögl, and R. Pentenrieder, Carbon **17**, 195 (1979); R. Pentenrieder and H. P. Boehm, Rev. Chim. Minéral. **19**, 371 (1982).
- [4] H. Selig, W. A. Sunder, M. J. Vasile, F. A. Stevie, and P. K. Gallagher, J. Fluor. Chem. **12**, 397 (1978).
- [5] A. A. Opalovskii, A. S. Nazarov, and A. A. Uminskii, Russ. J. Inorg. Chem. **17**, 1366 (1972).
- [6] Yu. I. Nikonorov and L. L. Gornostaev, Izv. Sib. Otd. Akad. Nauk S.S.S.R., Ser. Khim. Nauk **1980**, 48; C. A. **94**, 113 684 (1981).
- [7] A. S. Nazarov, V. G. Mokotchenko, and I. I. Yakovlev, Russ. J. Inorg. Chem. **23**, 925 (1978).
- [8] A. S. Nazarov, I. I. Yakovlev, A. F. Antimonov, V. M. Grankin, V. B. Durasov, and P. P. Semyanikov, Russ. J. Inorg. Chem. **25**, 836 (1980).
- [9] Yu. I. Nikonorov and B. I. Obmoin, Russ. J. Inorg. Chem. **25**, 839 (1980).
- [10] Yu. I. Nikonorov, N. G. Khainovskii, and E. F. Khairtdinov, Izv. Akad. Nauk S.S.S.R., Neorg. Mat. **21**, 1952 (1985); C. A. **104**, 43 900 (1986).
- [11] A. Hamwi, M. Daoud, and J. C. Cousseins, Synth. Met. **26**, 89 (1988).
- [12] W. Spiessler, doctoral thesis, Univ. Tübingen (1960).
- [13] A. A. Opalovskii, A. S. Nazarov, A. A. Uminskii, and Yu. V. Chichagov, Russ. J. Inorg. Chem. **17**, 1227 (1972).
- [14] Yu. I. Nikonorov and L. L. Gornostaev, Izv. Sib. Otd. Akad. Nauk S.S.S.R., Ser. Khim. Nauk **1979**, 55; C. A. **92**, 87 294 (1980).
- [15] Yu. I. Nikonorov, I. A. Poroshina, and E. L. Zhuzhgov, Izv. Akad. Nauk S.S.S.R., Neorg. Mat. **20**, 506 (1984); C. A. **101**, 103 005 (1984).

- [16] R. Vangelisti and A. Hirold, *Carbon* **15**, 327 (1977).
- [17] H. Takenaka, M. Kawaguchi, M. Lerner, and N. Bartlett, *J. Chem. Soc. Chem. Commun.* **1987**, 1431.
- [18] W. Rüdorff and G. Rüdorff, *Z. Anorg. Allg. Chem.* **253**, 281 (1947).
- [19] K. O. Christe and W. Sawodny, *Z. Anorg. Allg. Chem.* **374**, 306 (1970).
- [20] H. Selig, H. H. Claassen, and J. H. Holloway, *J. Chem. Phys.* **52**, 3517 (1970).
- [21] D. H. Brown, K. R. Dixon, C. M. Livingston, R. H. Nuttal, and D. W. A. Sharp, *J. Chem. Soc. (London)* **A 1967**, 100.
- [22] K. O. Christe and J. P. Guertin, *Inorg. Chem.* **4**, 905 (1965).
- [23] H. Touhara, K. Kadono, Y. Fujii, and N. Watanabe, *Z. Anorg. Allg. Chem.* **544**, 7 (1987).