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Synthesis and Charaterisation of Chromium Oxyselenide ($Cr_2Se_{0.7}O_{2.3}$) Formed from Chemical Vapour Synthesis: A New Antiferromagnet

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Chromium oxyselenide $Cr_2Se_{0.71}O_{2.30}$ was synthesised by chemical vapor synthesis of chromium oxychloride and diethyl selenide. The material adopts the Cr_2Se_3 structure type with a = 6.26(3) Å and c = 17.45(3) Å. The Raman spectrum shows bands at 225 and 550 cm^{-1}. X-ray photoelectron spectroscopy and wavelength dispersive analysis by X-rays confirmed the material was homogeneous and of uniform composition $Cr_2Se_{0.71}O_{2.30}$. The material is an antiferromagnet with a Neel temperature of 43 K. This is the first solid-state chromium oxyselenide reported and shows that the hard oxygen and soft selenium can co-exist in the same lattice if formed under the kinetic product conditions of a rapid gas-phase reaction.

Introduction

Chromium mixed chalcogenides have been thoroughly investigated by various workers over many years because of their interesting magnetic properties. The synthesis and magnetic properties of chromium sulfoselenide,[1] chromium sulfotelluride[2–4] and chromium selenotelluride[5,6] have been widely reported for a range of different compositions.[7,8] In contrast, only one paper reports the existence of a chromium oxysulfide, Cr_2S_2O,[9] neither chromium oxyselenide or oxytelluride phases are known. Indeed this is often a common pattern in solid-state transition metal chemistry where in polarisability terms the "hard" oxygen and "soft" selenium find it difficult to coexist in a solid solution without phase segregation or formation of layered materials in which the oxide and selenide blocks are separated. This is not to say that metal oxide-selenide solid solutions cannot exist, rather that by the conventional synthesis they invariably produce the thermodynamic product. A large number of phases have been reported in the chromium-selenium system and include Cr_5Se_8,[10] $CrSe_2$,[11,12] $CrSe_3$[13] and a series of compounds CrSe,[14,15] Cr_7Se_8,[16] Cr_5Se_6,[17] Cr_3Se_4,[18] and Cr_2Se_3 with the NiAs-type crystal structure, in which chromium vacancies are ordered. Cr_2Se_3 has a rhombohedral-type superstructure, which leads to complex antiferromagnetic arrangements below the Néel temperature T_N = 43 K.[19] An order-order magnetic transition is also known to occur at T_t = 38 K. The chromium-oxygen system is simpler than the chromium-selenium one, the most common phase being Cr_2O_3.[20] This phase is also an antiferromagnet with T_N = 307 K. Chromium(III) selenide has found applications such as protective films, black matrix films in liquid crystal displays, solar thermal energy collectors, in catalysis and in tunnel junction barriers.[21,22] Here we present the first report of the existence of a chromium oxyselenide phase formed from a rapid gas phase synthesis route, we hypothesise that the reason we can obtain an oxyselenide in this case is that the reaction is a fast and that we effectively "trap-out" the kinetic product.

Results and Discussion

Chromium oxyselenide was prepared from the atmospheric pressure chemical vapour deposition (APCVD) reaction of chromyl chloride and diethylselenide. Synthesis was accomplished under a dinitrogen atmosphere (99.99%) in a horizontal-bed cold-wall APCVD reactor heated to 600 °C. Et_2Se and CrO_2Cl_2 were preheated to 70 °C and 75 °C in their respective bubblers before being introduced into gas stream of hot N_2. They were then passed through a mixing chamber heated to 200 °C and were introduced into the reactor chamber. Chromyl chloride reacts in the gas phase with diethyl selenide to form a black fine powder that collects on the glass substrate. This can be readily removed by brushing with a fine hair-brush. Notably the same reaction at lower substrate temperatures of 400–550 °C forms a green adherent crystalline chromium oxide film and not the black chromium oxy-selenide powder.

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Scanning electron microscopy (SEM) images show a single morphological type of spherical nanoparticles with a mean size of 100 nm (Figure 1). Energy and wavelength-dispersive X-ray analysis (EDX/WDX) show that the powder contains chromium, oxygen and selenium. The elemental stoichiometry of the particles was determined to be $Cr_2Se_{0.71}O_{2.30}$ and the chlorine and carbon levels within the powder were found to be below the detection limit of the instrument (less than 0.5 atom-%). The sample was homogeneous by spot EDX analysis.

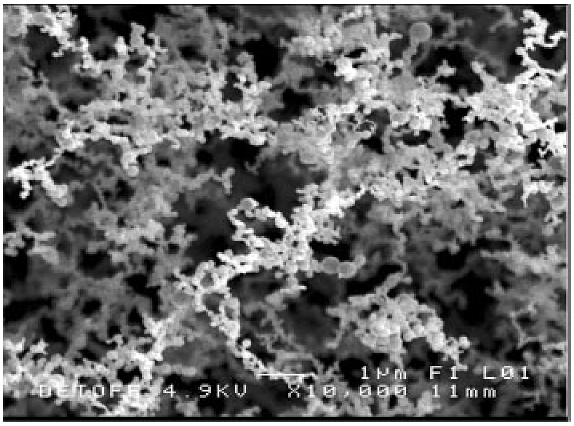

Figure 1. Scanning electron micrograph of the powder produced from the gas phase reaction of CrO_2Cl_2 and Et_2Se at 600 °C.

Powder X-ray diffraction (Figure 2) confirmed that the product from the gas-phase reaction is single-phase, crystalline and matches the reported pattern for rhombohedral Cr_2Se_3 (JCPDS File No. 040-1403).[19] The lattice parameters were calculated as a = 6.26(3) Å and c = 17.45(3) Å. Notably no chromium oxide was detected by powder diffraction. It has been shown previously that APCVD of chromyl chloride produces crystalline chromium oxide films at the same temperature of deposition (ca. 600 °C).[22–24]

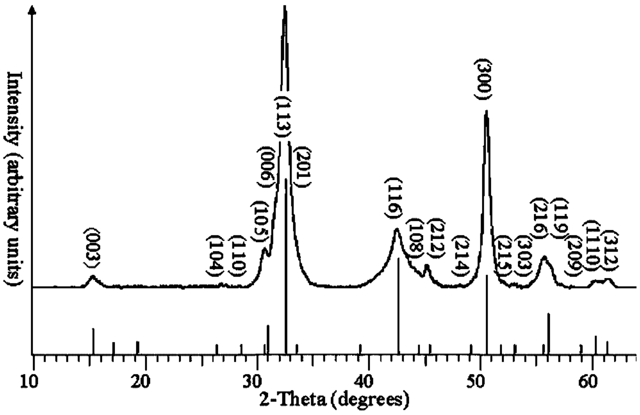

Figure 2. XRD pattern obtained for the powder formed from the APCVD reaction of CrO_2Cl_2 and Et_2Se at 600 °C. Literature stick pattern for rh-Cr_2Se_3 powder (JCPDS file No. 040-1403) is shown.

X-ray photoelectron spectroscopy of the as-prepared powder (Figure 3) shows the presence of three elements – chromium, oxygen and selenium in the same ratio as found from EDX analysis ($Cr_2Se_{0.7}O_{2.3}$). A single environment can be seen for each element; Cr $2p_{1/2}$ = 583.3 eV, Cr $2p_{3/2}$ = 576.2 eV; O 1s = 531.5 eV; Se $3d_{3/2}$ = 55.1 eV and Se 3d = 54.0 eV. The chromium environment for the $2p_{3/2}$ peak is intermediate between that of Cr_2O_3 at 576.6 eV and Cr_2Se_3 at 574.6 eV and indicative of Cr^{III}.[25,26] The oxygen 1s environment shows a narrow full width half maximum peak at 1.7 eV – indicative of a single environment with a binding energy shift consistent with an oxide and 0.7 eV close to that in chromium oxide 530.8 eV.[27] The selenium $3d_{3/2}$ peak matches that found in Cr_2Se_3 at 54.0 eV.[25]

Raman analysis of the powder (Figure 4) reveals broad bands at 225 cm^{-1} and 550 cm^{-1}. The absence of the distinctive (relatively intense) Cr_2O_3 Raman bands at 307, 350, 524, 551 and 610 cm^{-1} or CrO_2 bands at 458, 570 and

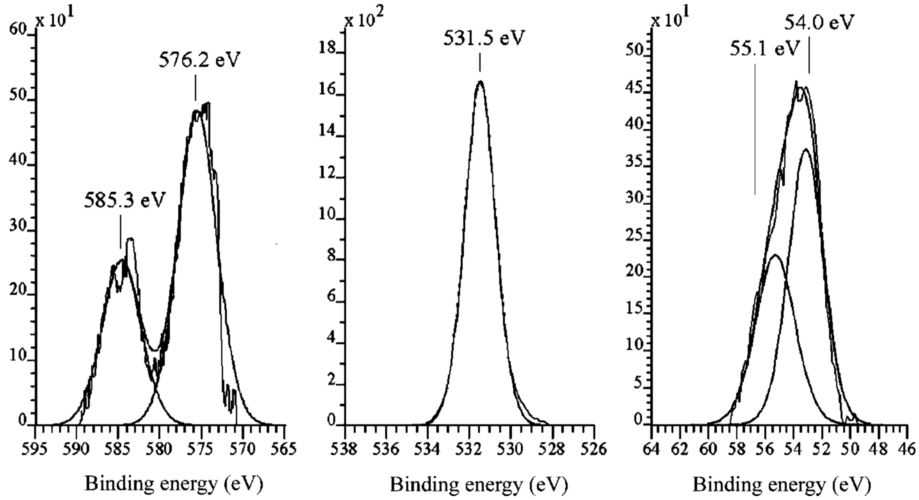

Figure 3. Selected area XPS spectra of the chromium oxyselenide powder produced at 600 °C from the gas phase reaction of CrO_2Cl_2 and Et_2Se. Left, Cr 2p region; middle, O 1s region; right, Se 3d region. Darker lines are the best fit and lighter lines the actual experimental data.

682 cm^{-1} (or indeed CrO_3) confirms that no chromium oxide was formed and co-doped during the gas-phase reaction of CrO_2Cl_2 and Et_2Se.[28,29]

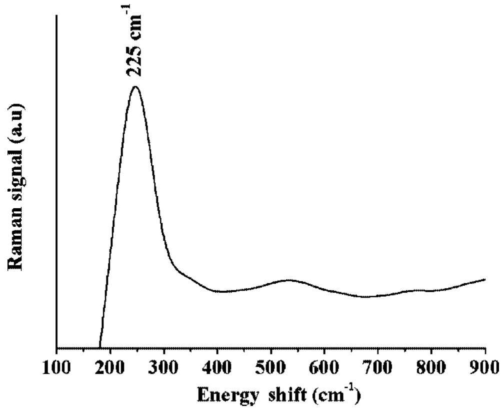

Figure 4. Raman pattern obtained for the powder formed from the gas phase reaction of CrO_2Cl_2 and Et_2Se at 600 °C.

The thermogravimetric analysis of $Cr_2Se_{0.7}O_{2.3}$ in air shows a gradual increase in weight of +24% between 60 °C and 420 °C. This is attributed to the oxidation of the selenium in the material to a selenate. A weight loss of –8% is observed from 420 °C to 550 °C corresponding to the decomposition of the selenate to form Cr_2O_3 and SeO_2 by loss of O_2. The second weight loss corresponding to –36% is seen from 600–800 °C and corresponds to the sublimation of all selenium in the form of SeO_2.[30]

The dc magnetic susceptibility (χ) as a function of temperature (Figure 5) shows a peak at 11 K. The large particle size (100 nm) precludes the possibility of this being due to a superparamagnetic blocking transition, and the substitution of oxygen with selenium is unlikely to generate any frustrated magnetic states. We therefore attribute the peak to an antiferromagnetic ordering transition. The Néel temperature at $T_N = 11$ K in $Cr_2Se_{0.7}O_{2.3}$ is less than that of Cr_2Se_3 ($T_N = 43$ K),[19] and much less that that of Cr_2O_3 ($T_N = 307$ K),[31] implying that the new material has somewhat different magnetic properties compared to its parent compounds.

The characterization data are all consistent with the formation of a hitherto unknown solid solution of $Cr_2Se_{0.7}O_{2.3}$ rather than the formation of two intimately mixed phases of Cr_2O_3 and Cr_2Se_3. SEM analysis shows a single type of particle morphology – spherical and agglomerated together – consistent with a gas-phase reaction, rather than two types of crystallite. WDX and EDX analysis show that the material is homogeneous to spot analysis with the same elemental formulation across the surface. The X-ray diffraction pattern shows a single-phase material of the Cr_2Se_3 structural type but with a larger unit cell. Previously we have shown that Cr_2O_3 is crystalline when prepared by CVD at 400 °C and adopts an adhesive film with angular crystallites.[22–24] Furthermore, we showed in this work at deposition temperatures from 450–600 °C a green chromium oxide film formed from reaction of Et_2Se and CrO_2Cl_2. It was only at 600 °C and above that a chromium oxyselenide phase formed, by gas-phase nucleation that "snowed" onto the surface to form a poorly adherent film that could be readily collected. The XPS analysis for the chromium oxyselenide showed only a single chromium environment rather than two well separated peaks for the oxide and selenide, furthermore the quantification of the element abundances matched the WDX analysis. The thermal gravimetric analysis results also correlate well with the elemental formula. The Raman pattern does not show any chromium oxide (corundum) in the powder but is consistent with a layered metal-selenide type structure. Furthermore the magnetic properties of the new material are unlike either – Cr_2Se_3 or Cr_2O_3 – which although both are antiferromagnets and have Néel temperatures of 43 and 307 K respectively. Hence there is strong evidence for the formation of a new chromium oxyselenide phase. We have yet to account for why the Néel temperature is depressed for the new oxyselenide phase compared to the end members of the series – however the magnetic structure of Cr_2Se_3 is extraordinarily complicated.[19] We are hopeful that by varying the reaction conditions it will be possible to make other compositions within the solid solution series CrO_xSe_y ($x + y = 3$). This work has shown that the "hard" oxygen and "soft" selenium can marry in the same chromium solid-state material without phase segregation. It also indicates that a fast gas-phase kinetic route could be the way forward for making a range of hitherto unknown oxyselenide phases.

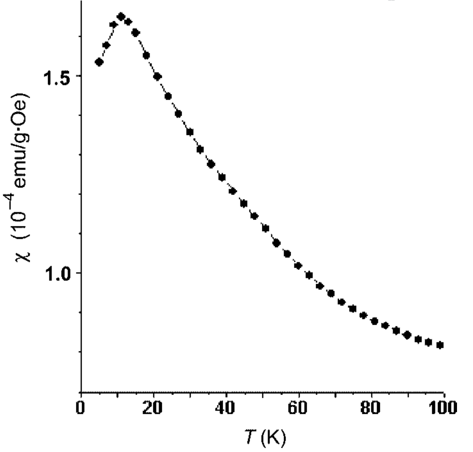

Figure 5. DC magnetic susceptibility (in a measurement field of 10 Oe) as a function of temperature for $Cr_2Se_{0.7}O_{2.3}$.

Experimental Section

Synthesis of the chromium oxyselenide nanoparticles was carried out under a dinitrogen atmosphere (99.99%) on glass substrates using a conventional horizontal bed cold-wall atmospheric pressure CVD reactor. The glass substrate was SiO_2 coated standard float glass (Pilkington, UK). The substrate was heated to 600 °C by a graphite block and the nitrogen carrier gas was preheated to 150 °C by being passed along 2 m lengths of coiled stainless steel tubing inside a tube furnace. The gases in the reaction were made to pass over the heated substrate and confined in position by a top plate that was ca. 4 mm above the substrate. After passage through the reaction chamber the gas stream was treated with bleach to destroy the possible presence of H_2Se and vented inside a fume cupboard.

Chromyl chloride was obtained form Strem and diethyl selenide was supplied by Aldrich. They were both used without further purification. The chromyl chloride and diethyl selenide were placed into two different stainless steel bubblers, which were respectively heated to 75 °C and 70 °C by an external jacket. They were both introduced into gas streams by passing hot N_2 through the bubblers. Flow rates of nitrogen through the CrO_2Cl_2 bubbler and Et_2Se were respectively 0.2 $L\,min^{-1}$ (3 $mmol\,min^{-1}$) and 2.0 $L\,min^{-1}$ (30 $mmol\,min^{-1}$) and the flow rate through the mixing chamber was kept constant to 3.0 $L\,min^{-1}$. Deposition time for the experiment was one minute. At the end of the deposition, the bubbler line was closed and the substrate was cooled under nitrogen in the reactor. Then the samples were collected on the substrate and handled briefly in air before storage in a dry oxygen-free nitrogen atmosphere in a glove box. It was subsequently found that the samples were air and water stable, so this procedure was not necessary.

X-ray diffraction patterns were measured on a Bruker AX5 B8 instrument using monochromated Cu-$K_{\alpha1}$ radiation ($K_{\alpha1}$ = 1.5406 Å). The diffractometer used glancing incident radiation (5°). The samples were indexed using Unit cell and compared to database standards. Wavelength dispersive X-ray and Energy dispersive X-ray analysis were obtained on a Philips XL30ESEM instrument and SEM was obtained on a JEOL 6301 instrument. Raman spectra were acquired on a Renishaw Raman System 1000 using a helium–neon laser of wavelength 632.8 nm. The Raman system was calibrated against the emission lines of neon. X-ray photoelectron spectroscopy was undertaken using a VG ESCALAB 220I XL instrument with focused (300 mm spot) monochromatic Al-K_α radiation at a pass energy of 20 eV. Scans were acquired with steps of 50 meV. A flood gun was used to control charging. Binding energies were referenced to an adventitious C 1s peak at 284.6 eV (this peak is due to residual pump oil used in the XPS high vacuum system, but is removed on the first argon ion etching). Argon sputtering was used for approximately 1 min in a rastering mode in order to remove surface contamination. Thermal gravimetric analysis (TGA) was performed with a heating rate of 10 °C$\,min^{-1}$ and on a Netzsch STA 449C instrument. Direct-current magnetic susceptibility measurements were performed using a commercial SQUID magnetometer (Quantum Design MPMS-XL) in a magnetic field of 10 Oe.

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[1] a) L. M. Doronina, V. S. Filatkina, S. S. Batsanov, *Neorg. Mater.* **1967**, *3*, 1696; b) V. N. Ikorskii, L. M. Doronina, S. S. Batsanov, *Zh. Struk. Khim.* **1968**, *9*, 143.

[2] S. S. Batsanov, L. M. Doronina, *Neorg. Mater.* **1966**, *2*, 491.

[3] V. N. Ikorskii, *Neorg. Mater.* **1973**, *9*, 938.

[4] a) M. Yuzuri, T. Yusuki, *J. Magn. Magn. Mater.* **1986**, *54*, 923; b) Y. Adachi, M. Yuzuri, T. Kaneko, S. Abe, *J. Magn. Magn. Mater.* **1990**, *90*, 153; c) Y. Adachi, M. Yuzuri, T. Kaneko, S. Abe, *J. Magn. Magn. Mater.* **1992**, *104*, 887; d) M. Yuzuri, Y. Adachi, T. Kaneko, H. Yoshida, S. Abe, *J. Magn. Magn. Mater.* **1995**, *140*, 151.

[5] M. Yuzuri, K. Segi, *Phys. B+C: Phys. Condens. Matt. + Atom., Mol. Plasma Phys.* **1977**, *86*, 891.

[6] S. Ohta, Y. Narui, Y. Sakayori, *J. Magn. Magn. Mater.* **1997**, *170*, 168.

[7] S. S. Batsanov, L. M. Doronina, *Ser. Khim.* **1968**, *9*, 2155.

[8] V. N. Ikorskii, S. S. Batsanov, *Neorg. Mater.* **1972**, *8*, 1858.

[9] S. S. Batsanov, L. M. Doronina, N. V. Podberezskaya, *Zh. Struk. Khim.* **1964**, *154*, 624.

[10] A. W. Sleight, T. A. Bither, *Inorg. Chem.* **1969**, *8*, 566.

[11] C. M. Fang, C. F. van Bruggen, R. A. de Groot, G. A. Wiegers, C. Haas, *J. Phys.: Condens. Matter.* **1997**, *9*, 10173.

[12] Y. Yoshida, K. Motizuki, *J. Phys. Soc. Jpn.* **1982**, *51*, 2107.

[13] a) S. J. Hibble, D. A. Rice, M. J. Almond, K. A. Hassan Mohammad, S. P. Pearse, J. R. Sagar, *J. Mater. Chem.* **1992**, *2*, 1237–1240; b) S. J. Hibble, R. I. Walton, D. M. Pickup, *J. Chem. Soc., Dalton Trans.* **1996**, *11*, 2245.

[14] M. Koyama, N. Happo, M. Tamura, J. Harada, T. Mihara, A. Furuta, M. Nakatake, H. Sato, M. Taniguchi, Y. Ueda, *J. Electron Spectrosc. Relat. Phenom.* **1996**, *78*, 83.

[15] L. M. Corliss, N. Elliott, J. M. Hastings, R. L. Sass, *Phys. Rev.* **1961**, *5*, 1402.

[16] T. Kaneko, J. Sugawara, K. Kamigaki, S. Abe, H. Yoshida, *J. Appl. Phys.* **1982**, *53*, 2223.

[17] H. Sato, M. Koyama, K. Takada, H. Okuda, K. Shimada, Y. Ueda, J. Ghijsen, M. Taniguchi, *J. Electron Spectrosc. Relat. Phenom.* **1998**, *88*, 333.

[18] M. Behrens, R. Kiebach, W. Bensch, D. Haeussler, W. Jaeger, *Inorg. Chem.* **2006**, *45*, 2704.

[19] a) Y. Adachi, M. Yuzuri, T. Kaneko, S. Abe, H. Yoshida, *J. Phys. Soc. Jpn.* **1994**, *63*, 369; b) Y. Adachi, M. Ohashi, T. Kaneko, M. Yuzuri, Y. Yamaguchi, S. Funahashi, Y. Morii, *J. Phys. Soc. Jpn.* **1994**, *63*, 1548; c) S. Ohta, Y. Adachi, T. Kaneko, M. Yuzuri, H. Yoshida, *J. Phys. Soc. Jpn.* **1994**, *6*, 2225.

[20] K. P. Lillerud, P. Kofstad, *J. Electrochem. Soc.* **1980**, *127*, 2397.

[21] P. M. Sousa, A. J. Silvestre, N. Popovici, O. Conde, *Appl. Surf. Sci.* **2005**, *247*, 423.

[22] a) A. Anguelouch, A. Gupta, G. Xiao, D. W. Abraham, Y. Ji, S. Ingvarsson, C. L. Chien, *Phys. Rev. B: Condens. Matt. Mater. Phys.* **2001**, *64*, 180408/1; b) A. Anguelouch, A. Gupta, G. Xiao, G. X. Miao, D. W. Abraham, S. Ingvarsson, Y. Ji, C. L. Chien, *J. Appl. Phys.* **2002**, *10*, 7140.

[23] I. P. Parkin, M. N. Field, *J. Phys. IV: Proceedings of the Twelfth Eur. Conf. on Chem. Vap. Dep.* **1999**, *1*, 387.

[24] a) W. J. DeSisto, P. R. Broussard, T. F. Ambrose, B. E. Nadgorny, M. S. Osofsky, *Appl. Phys. Lett.* **2000**, *76*, 3789; b) Y.-N. Cho, W. J. DeSisto, *Chem. Vap. Dep.* **2003**, *9*, 121.

[25] E. Agostinelli, C. Battistoni, D. Fiorani, G. Mattogno, M. Nogues, *J. Phys. Chem. Solids* **1989**, *50*, 269.

[26] C. D. Wagner, in *Pratical Surface Analysis Second Edition* (Eds.: D.Briggs, M. P.Seah), Wiley, Salle-Sauerlander, **1990**, vol. 1, p. 606–610.

[27] I. Ikemoto, K. Ishii, S. Kinoshita, H. Kuroda, M. A. A. Franco, J. M. J. Thomas, *J. Solid State Chem.* **1976**, *17*, 425.

[28] S. Kikuchi, K. Kawauchi, M. Kurosawa, H. Honjho, T. Yagishita, *Anal. Sci.* **2005**, *21*, 197.

[29] J. Mougin, T. Le Bihan, G. Lucazeau, *J. Phys. Chem. Solids* **2001**, *62*, 553.

[30] S. M. Grigorovich, A. V. Novoselova, Y. M. Ukrainskii, *Neorg. Mater.* **1975**, *11*, 2125.

[31] B. N. Brockhouse, *J. Chem. Phys.* **1953**, *21*, 961.

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