presence of M-OH and M-OH_2 absorptions in the relevant regions of the spectrum confuse the identification of forbidden bands and of any splittings of degeneracy.

Acknowledgements. The author wishes to thank Mr V. T. Rae, of Thornbury, who found and submitted the original material, Mr 'Sam' Weller of Pendeen for further samples and for information regarding the origin of material, and Mr B. V. Cooper of Torquay Natural History Museum for research and field investigations defining the location of origin, and collection of material. Thanks are also due to Mr K. Walkling of the Chemistry Department, U.M.I.S.T. for running PE 783 spectra to 200 cm^{-1}, and to Dr G. Ryback for helpful suggestions.

References

Braithwaite, R. S. W. (1983) *Mineral. Mag.* **47,** 51–7.
Cabannes-Ott, C. (1957) *C.R. Acad. Sci. Paris,* **244,** 2491–5.
Dines, H. G. (1956) *The Metalliferous Mining Region of South-West England,* **1,** Mem. Geol. Survey of Great Britain, 410.
Dufet, H. (1900) *Bull. Soc. fr. Min.* **23,** 147–50.
Frueh, A. J., and Golightly, J. P. (1967) *Can. Mineral.* **9,** 51–6.
Gamo, I. (1961*a*) *Bull. Chem. Soc. Japan,* **34,** 760–4.
——(1961*b*) Ibid. **34,** 764–6.
Goldsmith, J. A., and Ross, S. D. (1968) *Spectrochim. Acta,* **24A,** 2131–7.
Jaggi, H. von, and Oswald, H. R. (1961) Ibid. **14,** 1041–5.
Johan, Z., Povondra, P., and Slánsky, E. (1969) *Am. Mineral.* **54,** 1–13.
Kermarrec, Y. (1964) *C.R. Acad. Sci. Paris,* **258,** 5836–8.
Levitt, S. R., and Condrate, R. A. Sr. (1970) *Am. Mineral.* **55,** 1562–75.
Lyon, R. J. P. (1962) *Evaluation of Infrared Spectroscopy for Compositional Analysis of Lunar and Planetary Soils.* NASA report, Stanford Research Institute, Menlo Park, California.
Moenke, H. (1962) *Mineralspektren,* **I.** Akademie-Verlag, Berlin.
——(1966) Ibid. **II.**
Nakagawa, I., and Shimanouchi, T. (1964) *Spectrochim. Acta,* **20,** 429–39.
Nakamoto, K. (1978) *Infrared and Raman Spectra of Inorganic and Coordination Compounds.* 3rd ed. John Wiley and Sons, New York.
Plyusnina, I. I., Granadchikova, B. G., and Voskresenskaya, I. E. (1969) *Kristallografiya,* **14,** 450–5.
Prask, H. J., and Boutin, H. (1966) *J. Chem. Phys.* **45,** 3284–95.
Ramamurthy, P., and Secco, E. A. (1970) *Can. J. Chem.* **48,** 3510–19.
Russell, A., and Claringbull, G. F. (1955). *Mineral. Mag.* **31,** xlv [M.A. **13,** 30] also reported in Spencer, L. J. (1955) *Mineral. Mag.* **31,** 791.
Schmetzer, K., Berdesinski, W., Bank, H., and Kroužek, E. (1976*a*) *Neues Jahrb. Mineral. Mh.* 418–25.
——Bank, H., Berdesinski, W., and Kroužek, E. (1976*b*) *Z. Deutsch. Gemmol. Gesell.* **25,** 195–8.
——————(1978) *J. Gemmol.* **16,** 86–90.
Todor, D. N. (1976) *Thermal Analysis of Minerals.* Abacus Press, Tunbridge Wells.
White, W. B., and Roy, R. (1964) *Am. Mineral.* **49,** 1670–87.

[*Manuscript received 1 September 1986; revised 18 November 1986*]

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KEYWORDS: ceruleite, infrared spectrum, Cornwall

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MINERALOGICAL MAGAZINE, DECEMBER 1987, VOL. 51, PP. 741–3

$Ag_{1.2}Sn_{0.9}Sb_3S_6$, a tin-bearing andorite phase

ANDORITE is considered to be a relatively common Ag-sulphosalt mineral, and in some deposits it forms the chief silver ore (Chace, 1948). By substitution between 2Pb and Ag+Sb or 3Pb and 2Sb+□, andorite shows compositional variations from its formula $PbAgSb_3S_6$ (Nuffield, 1945; Mozgova *et al.*, 1983). In the system Ag_2S-PbS-Sb_2S_3, andorite displays an extensive range of solid solution at temperatures between 300 and 500 °C (Hoda and Chang, 1975). An andorite-like phase was synthesized in the study of reactions of silver sulphantimonides and tin sulphides (Chang, 1983). The purpose of this investigation is to examine its stability in the system Ag_2S-SnS-Sb_2S_3, and its relations to andorite.

Experimental procedures. Experiments were performed by means of the conventional evacuated glass capsule technique using specpure elements

(Pb, Sn, Sb, and S) and pure sulphide (Ag_2S). Heat treatment was conducted in muffle furnaces controlled to ± 3 °C. Quenched products were examined by X-ray powder diffraction and reflected-light microscopy. Chemical compositions of selected samples were determined by microprobe analysis. A peak stripping technique was used to compensate for the line overlaps of Sb and Sn. Cell dimensions of ± 0.02 Å were computed by using a least-squares refinement program.

Phase relations in the system Ag_2S–SnS–Sb_2S_3. A pair of intermediate phases is known to exist in each of the binary systems Ag_2S–Sb_2S_3 and SnS–Sb_2S_3, whereas the system Ag_2S–SnS has a simple eutectic relationship. $AgSbS_2$ and Ag_3SbS_3 melt congruently at 520 and 485 °C, respectively, and the system Ag_2S–Sb_2S_3 becomes completely solidified when the liquid phase on the antimony-rich side terminates at 450 °C (Keighin and Honea, 1969). $SnSb_2S_4$ melts incongruently at 493 °C to liquid and $Sn_3Sb_2S_6$, which in turn melts incongruently at 565 °C to liquid and SnS (Sachdev and Chang, 1975). Both $SnSb_2S_4$ and $Sn_3Sb_2S_6$ are orthorhombic with $a = 25.641$, $b = 20.381$, and $c = 3.8973$ Å (Smith and Parise, 1985) and $a = 23.18$, $b = 3.965$, and $c = 34.93$ Å (Smith, 1984), respectively.

Phase relations based on experimental data in the system Ag_2S–SnS–Sb_2S_3 at 400 °C are illustrated in Fig. 1. The system is divided into two halves by the join $AgSbS_2$–SnS, along which mutual solid solutions exist. $AgSbS_2$ at 400 °C has the NaCl-type structure, and its solid solution extends to $Ag_{0.9}Sn_{0.2}Sb_{0.9}S_2$. The solid solution of SnS has a range to $Ag_{0.1}Sn_{0.8}Sb_{0.1}S$.

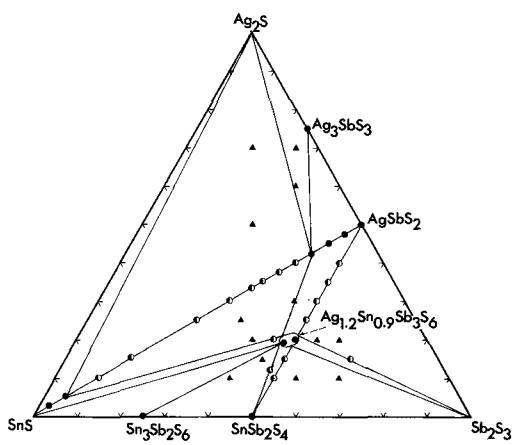

FIG. 1. Phase relations in the system Ag_2S–SnS–Sb_2S_3 at 400 °C. Symbols used are solid triangle, three phases; half-filled circle, two phases; and solid circle, one phase.

The andorite-like phase (Chang, 1983) is stable in the system, and forms equilibrium assemblages with SnS, $Sn_3Sb_2S_6$, $SnSb_2S_4$, Sb_2S_3, and $AgSbS_2$. Its composition, $Ag_{1.2}Sn_{0.9}Sb_3S_6$, falls on the join $AgSbS_2$–$SnSb_2S_4$, and correlates well with the composition of andorite, $AgPbSb_3S_6$. The substitution involves the following exchange: $Ag_{1.2} + Sn_{0.9} = Ag_{1.0} + Pb_{0.1}$, $Ag_{1.2}Sn_{0.9}Sb_3S_6$ melts congruently at 433 ± 2 °C, and has eutectic relations with $AgSbS_2$ and $AnSb_2S_4$. The eutectic temperatures determined in both relations are 427 ± 2 °C. The difference, if there is one, between them cannot be detected because the temperature range involved is very small. The compositions at the eutectic points are 45 and 57 mole% $SnSb_2S_4$.

Phase relations of tin-bearing andorite and andorite. A complete solid solution series exists between the tin-bearing andorite phase ($Ag_{1.2}Sn_{0.9}Sb_3S_6$) and andorite ($AgPbSb_3S_6$) as shown in Fig. 2 with melting points ranging from 433 to 506 °C. The curvature of the concave liquidus is greater than that of the solidus, which in fact has a tendency to become concave, resulting in an inflected curve. This feature suggests that andorite has a larger heat of fusion. The cell dimensions of this series vary within a very small range from $a = 13.04$, $b = 19.17$, and $c = 4.29$ Å for andorite to $a = 12.89$, $b = 19.15$, and $c = 4.22$ Å for tin-bearing andorite.

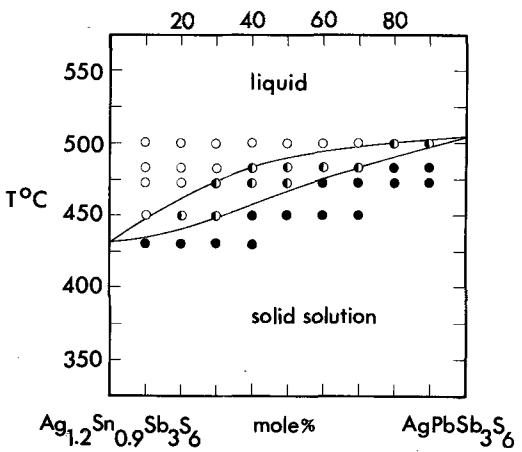

FIG. 2. Phase relations between tin-bearing andorite and andorite.

Non-occurrence of natural tin-bearing andorite. No tin-bearing andorite has been reported in nature. In the tin district of Bolivia, where andorite is the most abundant silver sulphosalt in the cassiterite–sulphide deposits, chemical analyses show the presence of Fe, Cu, and Zn in andorite

(Nuffield, 1945), but no Sn was reported. At Dachang, China, another cassiterite–sulphide deposit, andorite in a much restricted occurrence has a composition of $Ag_{0.96}Pb_{1.27}Sb_{3.03}S_6$ containing no tin (Huang, 1985). It appears that in these deposits the Sn present in the ore-forming environment formed tin minerals at relatively high temperatures, while andorite is a product of late-stage processes at lower temperatures. Recent analyses of andorite from various occurrences (Borodaev *et al.*, 1971; Birch, 1981; Makovicky and Mumme, 1983 and Moelo, 1983) all show an absence of Sn.

References

Birch, W. D. (1981) *Mineral. Mag.* **44,** 73–8.

Borodaev, Yu. S., Sveshnikova, O. L., and Mozgova, N. N. (1971) *Dokl. Akad. Nauk SSSR,* **199,** 1138–41.

Chace, F. M. (1948) *Econ. Geol.* **43,** 435–70.

Chang, L. L. Y. (1983) *13th Intern. Mineral. Association Program,* 249–59.

Hoda, S. N., and Chang, L. L. Y. (1975) *Am. Mineral.* **60,** 621–33.

Huang, M. Z. (1985) *Acta Geol. Sinica,* **3,** 240.

Keighin, G. W., and Honea, R. M. (1969) *Mineral. Deposita,* **4,** 153–77.

Makovicky, E., and Mumme, W. G. (1983) *Neues Jahrb. Mineral. Abh.* **147,** 58–79.

Moelo, Y. (1983) *Serie Documents BRGM,* **55,** 1–149.

Mozgova, N. N., Bortnokov, N. S., Organova, N. I., Tsepin, A. I., Kuz'mina, O. V., and Nekrasov, I. Ya. (1983) *Mineral. Zhur.* **5,** 17–33.

Nuffield, E. W. (1945) *Trans. R. Soc. Can. Series III,* **39,** 41–9.

Sachdev, S. C., and Chang, L. L. Y. (1975) *Econ. Geol.* **70,** 1111–22.

Smith, P. P. K. (1984) *Acta Crystallogr.* **C40,** 581–4.

—— and Parise, J. B. (1985) Ibid. **B41,** 84–7.

[*Manuscript received 3 November 1986; revised 29 December 1986*]

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KEYWORDS: andorite, tin, silver, sulphosalt.

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MINERALOGICAL MAGAZINE, DECEMBER 1987, VOL. 51, PP. 743–6

An unusual form of coated diamond

SOME naturally occurring diamonds have an outer layer which is somewhat opaque and coloured. These diamonds are known in the trade as coated diamonds, and are of some interest as their unprepossessing exterior may conceal a core of good quality diamond (Bruton, 1970; Copeland, 1960; Custers, 1950; Lonsdale and Milledge, 1965; Orlov, 1977). Generally they are easily recognized by their lack of transparency, apparently arising from the presence of some impurities. Other methods of inspection reveal fundamental differences in the structure of core and coat. X-ray topographs commonly indicate the presence of patterns of structure in the core formed by growth on {111} planes, whereas the patterns in the coat are quite different, and suggestive of some form of radial growth (Kamiya and Lang, 1965; Machado *et al.*, 1985). Coated diamonds also show very characteristic behaviour when viewed in the cathodoluminescent mode (CL) of the SEM, the luminescence of coat and core differing greatly both in form and intensity.

We have recently examined seven natural colourless diamonds of gem quality from Zaire. They are of dodecahedral form and exhibit some vestigial {111} surfaces which permit a view into the interior of the stone. Visual and microscopic inspections of these diamonds gave no suggestion that the crystals were of other than uniform composition. However, on polishing an (001) surface on one of them (A52) for an experiment to be described elsewhere, a marked step was observed on the surface between the central and outer regions; see Fig. 1, an optical micrograph taken with Nomarski technique. The stone was then examined by X-ray topography and in the SEM. Fig. 2, a section topograph of this diamond shows a central pattern of growth typical of perhaps most diamonds, and an outer radial pattern similar to that observed in coated stones. Fig. 3 shows micrographs of the same diamond taken in the CL mode of the SEM with exposure chosen to bring out detail of the coat and core respectively. Note in particular the absence of linear growth lines in the coat and the indications