A ^{133}Cs-NMR Study of the Chemical Bonding of the Solid Compound Semiconductor Cs_3Sb

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^{133}Cs nuclear magnetic resonance has been studied in the solid compound semiconductor Cs_3Sb between room temperature and the melting point. From the magnitude of the chemical shift (620 ± 25 ppm at 300 K) and the quadrupolar coupling constant ($e^2qQ/h = 105 \pm 3$ kHz) we conclude that predominantly ionic bonding does not occur in this semiconductor.

Introduction

The alkali-antimonide compounds are of some technical importance because of their high photoelectric quantum efficiency in the visible region. For this reason the electronic properties of these semiconductors have been studied relatively intensively in the past — for comprehensive reviews see Ref. [1] and [2] —. However, the understanding of the nature of chemical bonding of these materials is less clear. The 3 : 1 compounds crystallize either in a hexagonal structure isotypic with that of Na_3As or in a cubic modification of either the BiF_3 or NaTl structure. Several of these compounds show a transition from cubic to hexagonal or vice-versa as the temperature is raised — see e.g. [2] — indicating only slight energy differences between these structures. In the case of Cs_3Sb only the cubic structure has been reported so far [3], where below 260 K De Munari et al. [4] suggest that there is an ordered arrangement of the Cs atoms with O_h^5 symmetry, although at room temperature it has been assumed by Jack and Wachtel [3] that the Cs-Sb sublattice is partially disordered.

The chemical bonding of all these compounds based upon these structures has until recently been described by resonating sp-hybridized bonds [5], [6]. However, in a recent series of XPS studies Bates et al. [7] have suggested that the bonding in Cs_3Sb is predominantly ionic in character in conflict with the previous assumptions of covalency in these compounds. In order to obtain further information on these questions we report here measurements of the ^{133}Cs NMR chemical shift, the spin-lattice relaxation time T_1, and the quadrupolar splitting of solid Cs_3Sb.

Experimental

Measurements were performed using a conventional home built pulsed NMR spectrometer at frequencies from 12—40 MHz. The Fourier transform of the free induction decay was obtained by sweeping the field or frequency through resonance whilst integrating the output of the spectrometer with a boxcar integrator [8]. A typical spectrum is shown in Fig. 1. The ^{133}Cs shift was determined relative to an aqueous CsCl solution corrected to infinite dilution [9]. Standard pulse techniques were used to obtain the spin-lattice relaxation time, T_1, and the spin-spin relaxation time, T_2, respectively.

Several different samples were investigated, most were made by reacting stoichiometric amounts of Cs and Sb in a sapphire NMR cell at high temperatures above the melting point of Cs_3Sb of 725 °C. One sample was bought from Cerac Com-

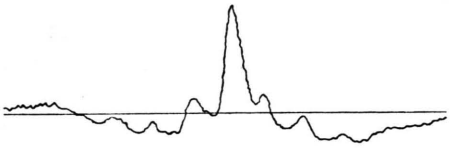

Fig. 1. An average frequency sweep (width 43 kHz) showing quadrupolar splitting of the ^{133}Cs-NMR resonance in solid Cs_3Sb at room temperature.

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pany [10], this had been prepared by precipitation from ammonia solution. X-ray investigation of this material showed diffuse spots at the Cs_3Sb positions. All samples were estimated to be within 0.1 atomic percent of stoichiometry.

Results and Discussion

The spectrum presented in Fig. 1 was obtained for the Cerac material and shows a clear quadrupolar splitting with a quadrupole coupling constant $e^2qQ/h = 105 \pm 3$ kHz and a chemical shift of 620 ppm. Most of the samples prepared from the melt showed only a single line with a shift between 585 and 640 ppm. The absence of quadrupolar splitting may be due to either larger deviations from stoichiometry or to the structure of these samples being partially disordered as was found by Jack and Wachtel [3]. However, the room temperature spin-lattice relaxation time, T_1, varied between 75 and 180 ms for the bulk samples compared with 30 ms for the Cerac material and a similar value for a bulk sample which showed quadrupolar splitting. Since this relaxation time was practically independent of temperature up to about 150 °C for all samples it is presumably due to paramagnetic impurities probably in the form of donor or acceptor impurities. Since the Cerac sample apparently contains more impurities, partial disorder seems the more likely explanation. The central peak in Fig. 1 apparently shows a slight asymmetry with respect to the quadrupolar pattern. This may reflect the two different Cs sites in the Cs_3Sb structure, one of which has cubic symmetry and therefore no splitting and possibly a slightly different shift from the other one. On the other hand from the observed quadrupolar splitting we conclude that some of the Cs sites have a local environment with non cubic symmetry which presumably results from a distortion of the structure.

When the temperature is raised above 100 °C, motional narrowing occurs in all samples and the quadrupolar splitting disappears. With increase of temperature above 250 °C the shift becomes temperature dependent and in general one or two additional lines of much lower intensity are observed. A minimum shift of ~ 300 ppm occurs around 500 °C, it then increases rapidly to reach a maximum of ~ 2000 ppm just below the melting point where the relaxation time T_1 is ~ 1.0 ms.

Both the chemical shift and the quadrupolar coupling constant give information about the chemical bonding in Cs_3Sb. Neither are consistent with predominantly ionic bonding as suggested by Bates et al. [7]. The magnitude of the chemical shift can be taken as a measure of the covalency of the bond [11]. Since the shift in Cs_3Sb is 620 ppm compared with 275 ppm for CsI [12] and 375 ppm for CsAu [13] it is clear that much higher p character is present in Cs_3Sb. In addition, the marked decrease of the shift with temperature up to 500 °C cannot be explained with an ionic model. The quadrupolar splitting is directly related to the electric field gradient at the ^{133}Cs nucleus. However, quantitative evaluation of the field gradient in order to obtain direct information about charge transfer is not worthwhile because the amount of structural distortion cannot be estimated. A qualitative idea of the size of the field gradient may be derived from a comparison with related alkali compounds, for instance, the quadrupolar coupling constant reported here lies between those of Li_3Sb and Na_3Sb [14] as it does in the alkali sulphates [12], [15], [16]. Ossman and McGrath [14] showed that the field gradient in Li_3Sb and Na_3Sb could not be explained by an ionic model, but by assigning an average charge of the order of 0.5 e on the alkali sites (using the Mooser-Pearson bonding scheme [17]) they could obtain the observed splitting.

Although the antimony compounds are not directly comparable because of their different structures it is clear that an appreciable electric field gradient exists in Cs_3Sb presumably at Cs sites which have both Cs and Sb nearest neighbours and this is incompatible with predominantly ionic bonding. These conclusions are consistent with recent calculations by Robertson [18] who, in a tight binding band structure calculation, estimated that the charge on the Cs sites in Cs_3Sb is 0.57 e.

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