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Electron Characteristic Energy Losses in Some Intermetallic Compounds[*]

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Measurements have been made of the characteristic energy losses of 30-kev electrons in transmission through thin films of indium, indium antimonide, cadmium telluride, and zinc telluride; for comparison, the electron energy losses in antimony, cadmium, tellurium, and zinc have been reinvestigated. The energy loss spectra in these intermetallic compounds appear significantly different from a simple superposition or average of the energy loss spectra of the component metals. Some detailed interpretations of the characteristic energy losses in In and in InSb are suggested.

INTRODUCTION

IN a previous study[1] a similarity was found between the electron energy loss spectra in some metals and the loss spectra in their oxides or sulfides. The same study showed only a slightly higher energy loss value in an intermetallic compound as compared to that in the less electronegative (i.e., the more metallic) component. However, the spectrum of the more electronegative component appeared definitely different from that of the intermetallic compound.

As these observations were made on compounds of the sodium chloride type of crystal structure, the present study was undertaken to determine whether the same behavior might be observed in intermetallic compounds having the zinc sulfide type of structure. In this study the electron characteristic energy losses were measured in the intermetallic and semiconducting compounds, indium antimonide, cadmium telluride, and zinc telluride, all of which have the same number of valence electrons and a mostly covalent chemical bonding. In addition, to obtain a more significant comparison between the energy loss values in these compounds and in each of their components, the energy losses were reinvestigated in antimony, cadmium, tellurium, zinc, and more particularly in indium, which had previously been studied only in reflection.[2]

EXPERIMENTAL PROCEDURE

Energy losses were observed by passing the electron beam through thin films. A Mollenstedt-type spectrometer, which has been described previously,[1] was used. The detecting device consisted of a fluorescent layer viewed by a photomultiplier tube. The accelerating voltage was 30 kv and the mean thickness of the specimens was of the order of 500 A. The solid films were self supported and, except for one zinc specimen, were prepared by vacuum deposition onto a cleaved rock salt substrate. They were then floated off on water and picked up on the specimen holder. The evaporation time was between 10 and 20 seconds. Some specimens of InSb were annealed by vacuum heating for two hours at 250°C.

RESULTS

Indium.—A total of 81 spectra were recorded and measured, using many different specimens from two separate evaporations. All these spectra show a main loss line at 20.5 ev, and often a weaker one at 5.7 ev (Fig. 1); there are also a few indications for an energy loss value around 12.5 ev, but only with the specimens of the second evaporation. These results are in fairly good agreement with the values previously measured in reflection by Kleinn (5.9, 12.2, and 22.3 ev).[2] However, the main loss line in the present study is at a lower energy. This main loss line is rather broad, with a mean width about four times the width of the zero loss line.

Antimony.—A main loss line was found at 15 ev, and another one at 29.8 ev, in good agreement with recent results (15.6 and 30.2 ev).[1]

Indium antimonide.—A total of 146 spectra were measured with specimens from two different evaporations. No significant differences were found using annealed specimens. Most of these spectra show only one loss line located at 13 ev. There are also a few indications of two other energy loss values around 19.5 and 24.3 ev, respectively (Fig. 2). The main loss line is much nar-

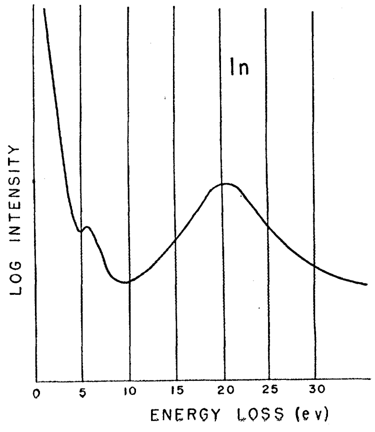

FIG. 1. Energy loss spectrum in indium.

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[1] L. B. Leder, Phys. Rev. **103**, 1721 (1956).

[2] W. Kleinn, Optik **11**, 226, (1954).

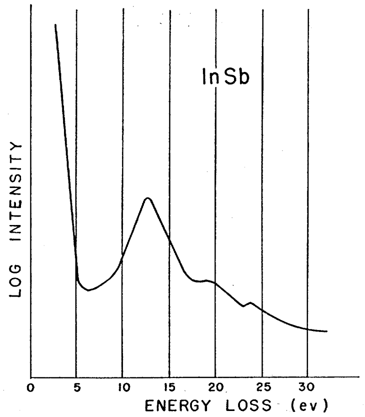

FIG. 2. Energy loss spectrum in indium antimonide.

rower than for indium; it is only about twice the width of the zero loss line.

Cadmium.—The thin films of this metal were prepared by vacuum deposition onto a rock salt substrate kept at liquid nitrogen temperature. The main loss line was found at 19.2 ev, in good agreement with a previously reported value of 18.7 ev.[3]

Tellurium.—The main loss line was found at 17.7 ev, in excellent agreement with a recently published value, 17.9 ev.[1]

Cadmium telluride.—A total of 117 spectra were measured, with specimens from two different evaporations. In most cases these spectra show only one loss line located at 16.9 ev. However, some records gave indications of a weaker loss line at 5.8 ev (Fig. 3). The main loss line is broad, and its mean width is about 3.5 times the width of the zero loss line.

Zinc.—Fifty spectra were measured using different specimens from two distinct evaporations. The films were condensed onto a rock salt substrate kept at liquid nitrogen temperature. The spectra show a main loss line at 17.8 ev, in reasonably good agreement with a previous value of 17 ev.[3] Another loss line was found at 13.8 ev, but there was only a slight indication of a first loss value around 5 ev, previously reported at 5.7 ev.[3] In order to check the possible influence of hydroxide formation during the immersion of specimens in water, the energy loss spectrum from a film evaporated onto a collodion substrate was recorded: no significant differences were found with this specimen.

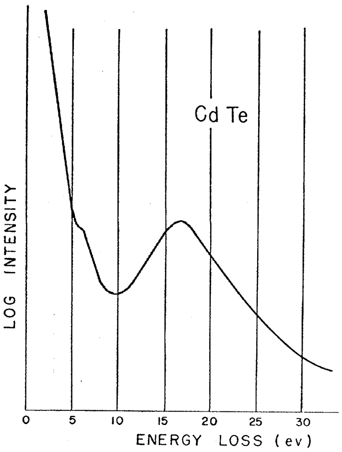

FIG. 3. Energy loss spectrum in cadmium telluride.

Zinc telluride.—A total of 81 spectra were measured, with specimens from three different evaporations.[4] The main loss line is located at 16.3 ev, and is about four times wider than the zero loss line. Another loss line is also clearly visible at 4.6 ev on almost every spectrum (Fig. 4). The experimental results are given in Tables I and II.

DISCUSSION

At present it is difficult to suggest a complete interpretation of the electron characteristic energy losses in each of the intermetallic compounds studied. However, it should be noted that all these spectra have one feature in common, i.e., that the main loss line in a given compound is not a simple superposition (either resolved or unresolved) of the main loss lines in each of the component metals. This result would seem to indicate that the character of the spectra is not determined by a sum of individual atomic contributions, but rather is due to the contributions from an aggregate of atoms. It appears that it is the crystalline lattice as a whole, or at least a group of neighboring atoms, which plays a dominant role in the electron energy loss process in these compounds.

More detailed, though tentative, interpretations will now be proposed for two cases: indium and indium antimonide.

Indium.—The calculated plasma frequency for all the valence electrons, including two 5s electrons and one 5p electron, is 12.6 ev. This value is in strong disagreement with the observed value (20.5 ev) of the main energy loss. This situation is in contrast with the case of aluminum, where the plasmon energy is calculated with the same number of valence electrons, i.e., three electrons per atom. The difference between the aluminum and the indium spectra can perhaps be understood because the

TABLE I. Measured energy loss values (in ev). The errors shown are standard deviations. The number of measurements is given in parenthesis after each energy loss value.

Material	Energy loss (ev)		
Indium	5.7 ±0.6 (42)	12.5 ±1.1 (16)	20.5 ±0.9 (81)
Antimony	15.0 ±0.5 (23)	29.8 ±0.3 (5)	
Indium antimonide	13.0 ±0.7 (146)	19.5 ±1.6 (45)	24.3 ±1.7 (20)
Cadmium	19.2 ±0.9 (46)		
Tellurium	17.7 ±1.1 (21)		
Cadmium telluride	5.8 ±0.7 (9)	16.9 ±0.8 (117)	
Zinc	5.0 ±0.9 (11)	13.8 ±0.5 (22)	17.8 ±0.9 (50)
Zinc telluride	4.6 ±0.4 (28)	16.3 ±0.7 (81)	

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[3] Leder, Mendlowitz, and Marton, Phys. Rev. **101**, 1460 (1956).

[4] The samples of ZnTe were kindly supplied by Edward L. Lind, RCA Laboratories, Princeton, New Jersey.

energy separation between the outside valence shell and the nearest core shell in free atoms is about 70 ev in aluminium, but only about 15 ev in indium. It is, therefore, very likely that the energy of some interband transition in metallic indium, such as for instance a 4*d*-5*sp* transition, is so close to the plasmon energy that it is no longer possible to consider the plasmons as independent excitation modes.

An attempt was therefore made to describe the energy loss spectrum in indium in terms of individual excitations of electronic interband transitions, and a comparison was made with the x-ray absorption data given by Sandstrom.[5] The energy separation between the L_{I} absorption edge and the first absorption maximum which follows was found by him to be 6 ev, which is very close to the loss value observed in this study at 5.7 ev. Thus, we may tentatively assume that the 5.7-ev loss is due to an electronic transition from the valence band toward an excited state in the empty part of the 5*p* band. It is also possible that the 20.5-ev loss is due to an electronic transition from the inner 4*d* band toward the same excited state, because the 4*d* level lies about 15 ev below the valence shell (Fig. 5). The comparison with the L_{II} and L_{III} absorption spectra is much more difficult and confused, mainly because these absorption edges show a complicated structure.

Indium antimonide.—It is suggested that the main loss line at 13 ev is due to the excitation of a valence band plasmon. This interpretation is compatible with the fact (particularly striking in the InSb spectrum) that in the compounds studied the main loss line is not a superposition of the main loss line in each of the two components. Futher observations supporting the same interpretation are as follows: (a) The main loss value is quite close to the calculated plasmon value (12.8 ev) obtained by including all the valence electrons (eight per molecule) in the plasma, and (b) the main loss line is fairly sharp.

CONCLUSIONS

The principal conclusion that may be derived from this work is that the electron energy loss spectra in the intermetallic compounds studied are significantly different from the loss spectra in both component metals. The case of InSb is especially striking in this respect, and the main loss value is here given accurately by the usual plasma frequency formula.

This general conclusion, which is in contrast with results for the other metallic compound spectra so far described,[1] does not appear to be in accordance with a purely atomic interpretation of these energy losses, but seems rather to favor some kind of collective interpretation. This feature may be associated with the covalent character of the chemical bonding or with the crystal lattice type.

In the case of indium, two energy loss values could be explained by individual excitations of electronic in-

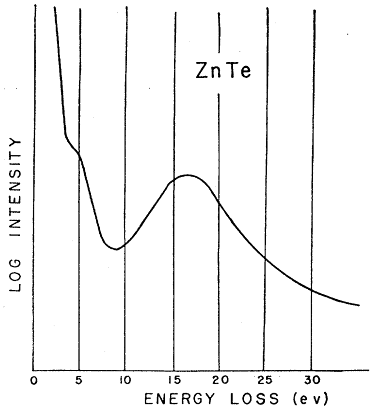

FIG. 4. Energy loss spectrum in zinc telluride.

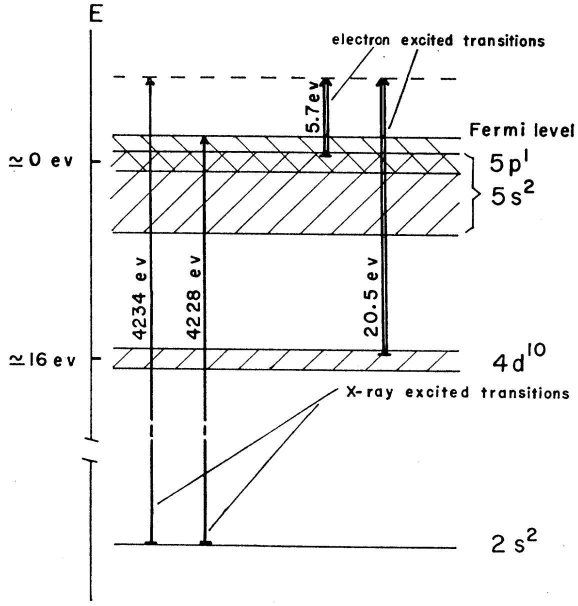

FIG. 5. Schematic energy band diagram for indium, together with the x-ray absorption transitions, and the transitions proposed as responsible for two electron energy losses.

TABLE II. Measured values and relative half-widths of the main loss lines. Γ/Γ_0 is the ratio of the half-width of the main loss line to the half-width of the zero loss line. $\hbar\omega_p$ is the plasmon energy calculated with n "free" electrons per atom or molecule; the usual number of s and p valence electrons is here chosen for n.

	ΔE(ev)	Γ/Γ_0	$\hbar\omega_p$(ev)	n
Indium	20.5	3.8	12.6	3
Indium antimonide	13.0	2.1	12.8	8
Cadmium telluride	16.9	3.5	13	8
Zinc telluride	16.3	3.8	14	8

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[5] A. Sandstrom, Nova Acta Regiae Soc. Sci. Upsaliensis 9, No. 11 (1935).

terband transitions. However, the results do not justify ruling out other possible processes.

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Effects of Dissolved Gas on the Superconducting Characteristics of Tantalum*

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The adding of a metallic impurity to a monatomic superconductor is a standard technique employed in experiments where it is desirable to vary systematically some of the material properties of the specimen, e.g., the mean free path or the penetration depth. While it has long been surmized that the addition of a gaseous impurity would produce comparable effects, there has, to our knowledge, been no systematic work carried out to verify this assumption or to measure the magnitude of the effects produced.

We here give a preliminary report on some recent work in which the concentration of a nitrogen contaminant in tantalum has been varied systematically. One effect of the nitrogen contaminant is striking. Very small amounts of gas allow, by a mechanism as yet unknown, for the formation of a "substructure" which permits superconducting inclusions to exist at fields considerably higher than the so-called critical field associated with flux exclusion in the bulk of the specimen. The general behavior of the contaminated specimens is basically the same as that observed in inhomogeneous alloys containing relatively large metallic impurity concentrations. Work is currently in progress to illuminate the basic mechanisms involved in the formation of a substructure in tantalum.

TANTALUM is one of a number of materials whose superconducting transition characteristics are strongly influenced by chemical and physical impurities and is, in many respects, an ideal material in which to investigate impurity effects.[1] Recent work by Connell and Seraphim[2] has shown that the general effect of impurities, as deduced from outgassing experiments, is to produce a superconducting substructure[3] which persists at fields considerably greater than the so called "critical field" associated with flux transitions in the bulk of the sample. This substructure manifests itself in measurements of the resistance of tantalum in the manner indicated in Fig. 1, which shows plots, reproduced from chart recordings of the variation of resistance of thin wire specimens with applied longitudinal field at a number of temperatures. The resistive transition is characterized by an initial rather sharp onset of resistance followed by a gradual restoration of resistance with increasing field. Independent but simultaneous measurements of the specimen susceptibility[2] indicate that the bulk of the flux transition occurs with the sudden onset of resistance and that the resistance subsequently restored can be associated with the destruction of superconductivity in inclusions which represent only a small fraction of the total volume of the specimen.

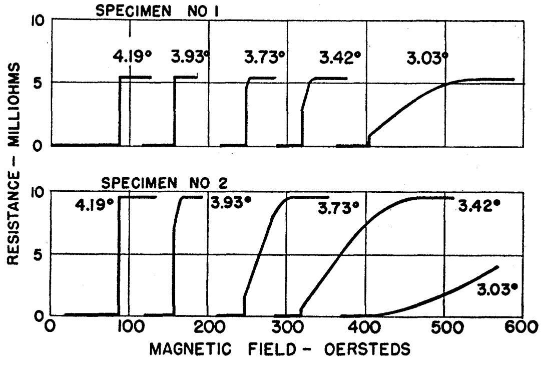

FIG. 1. Plots of specimen resistance as a function of the applied longitudinal magnetic field for two tantalum wires. 1(a) contains 1.53×10^{-3} atomic percent nitrogen, 1(b), 1.53×10^{-2} atomic percent nitrogen. All measurements were made with a measuring current of 45 milliamperes.

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† On leave from the Philips Research Laboratories, Eindhoven, Holland.

[1] Budnick, Ittner, and Seraphim, presented at the Sixth International Conference on Low-Temperature Physics and Chemistry, Leiden, June, 1958 (unpublished). A number of papers resulting from this work will be published shortly.

[2] R. A. Connell and D. P. Seraphim, Bull. Am. Phys. Soc. Ser. II, 3, 383 (1958) (to be published in detail).

[3] This sort of behavior is not new. Its appearance in alloys was interpreted by Mendelssohn as the result of a matrix of superconducting filaments which formed a "sponge" within the normal material. We prefer to speak more generally of the effect as being due to a substructure which may under certain circumstances result in the formation of real physical filaments but which appears to be caused by imperfections and impurities which are not necessarily distributed as filaments.