perature resistivity,[3] are concave monotonically increasing functions of $n_f$; (2) $\chi(0) \sim \gamma$ and $\chi(0) \sim T_{s.f.}^{-1}$; and (3) the $\chi T$ vs $\ln T$ behavior predicted by Krishna-murthy, Wilkins, and Wilson[14] in the $U \gg \Gamma$ regime is qualitatively verified. The origin of the 6-K specific-heat bump is not known. Finally, it should be noted that thermodynamic arguments by de Boer *et al.*[19] suggest that $CeRh_3$ may not be tetravalent and hence disagree with the results reported here.

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## Field-Ion Emission from Liquid Tin

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The ion emission from a field-produced Taylor cone on a molten tin surface is found to consist of many atomic and molecular species, the abundance of which is analyzed by mass spectroscopy. The energy spectra for these different ions have been measured for several emission currents, providing information about the mechanism of ion production. The behavior of the energy spread is discussed in terms of Coulomb interactions in the beam.

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Liquid-metal field-ion sources provide great promise in the field of ion beam microfabrication,[1] as a consequence of their high emission current (1–100 $\mu$A) and small emitting area. In a standard source a needle of appropriate material (usually tungsten) sharpened to a point of radius $\simeq$1–10 $\mu$m is connected to a heated reservoir containing the metal of interest. By suitable wetting, a film of molten metal can flow to the tip. Ion emission occurs when a sufficient positive voltage is applied to the needle so that the liquid on the apex is deformed into a cone—the Taylor cone[2]—of semiangle 49.3°.

Most experimental investigations have concerned gallium ion sources[3–6] in which case the dominant ion species is $Ga^+$. Other metals such as gold,[7,8] cesium,[9,10] and alloys[11] have also been studied; for them the mass spectrum is much more complex with multicharge and molecular ion species.

This Letter presents results of an experimental investigation of a liquid-tin ion source, a metal which does not seem to have been studied so far. The source comprises a small coil of tungsten wire acting as a reservoir of molten tin from which protrudes a tungsten needle wetted by a film of liquid metal.[12] By varying the applied voltage between tip and extractor from typically 5 to 8 kV, the total current increases regularly from 1 to 70 $\mu$A. Moreover the ion source is mounted in such a way that the distance between the emitting point and the extracting electrode can be varied. The emission current can therefore be altered without changing the extraction voltage or any other setting of an analyzer.

The energy and mass distributions of individual ion species have been measured with a double-focusing mass spectrometer consisting of an electrostatic sector followed by a magnetic analyzer. Figure 1 shows a mass spectrum obtained at very low current ($I_t = 1$ $\mu$A) and the relative abundance of identified species is reported in Table I. The mass resolution is adequate to resolve the different isotopic combinations up to at least cluster $n = 7$. There are ten stable isotopes of tin and for ions $Sn^{++}$, $Sn^{+}$, and $Sn_2^{+}$ all expected peaks have been detected with their relative intensity. Such mass spectra are extraordinarily rich in different species, and signals corresponding to heavier clusters have been recorded, but not yet clearly identified except for single-charge clusters with $n$ ranging to 11. A general observation is that the relative abundance of large clusters with respect to small ones decreases as the total emitted current grows. This behavior is illustrated in Table I which also contains the data for a source working in a high emission current. It should be emphasized that the cluster intensities are far in excess of those found in electron ionization of a vapor of tin in thermodynamic equilibrium with the liquid, for which, for example, the ratio $Sn_6^{+}/Sn^{+} = 10^{-6}$.[13]

To record an energy-loss spectrum a bias voltage is applied to both tip and extractor so as to keep constant the emission current while scanning the spectrum. Figure 2 shows some typical energy distributions for $Sn^{+}$ and $Sn^{++}$ at different emission currents. The absolute energy scale has been calibrated by recording the energy spectrum of $Sn^{+}$ issued from a frozen Taylor cone. In this case, similarly to what has already been observed for gold, a low current (less that $10^{-9}$ A) is emitted from self-sharpening protuberances on the frozen Taylor cone surface.[14] It seems most likely that ion emission from the frozen cone is by field evaporation. The maximum in the energy distribution (with respect to the applied voltage) is therefore given, to a good approximation, for $Sn^{+}$ by

$$e\Delta V_c \approx I_1 + \Lambda - \varphi. \quad (1)$$

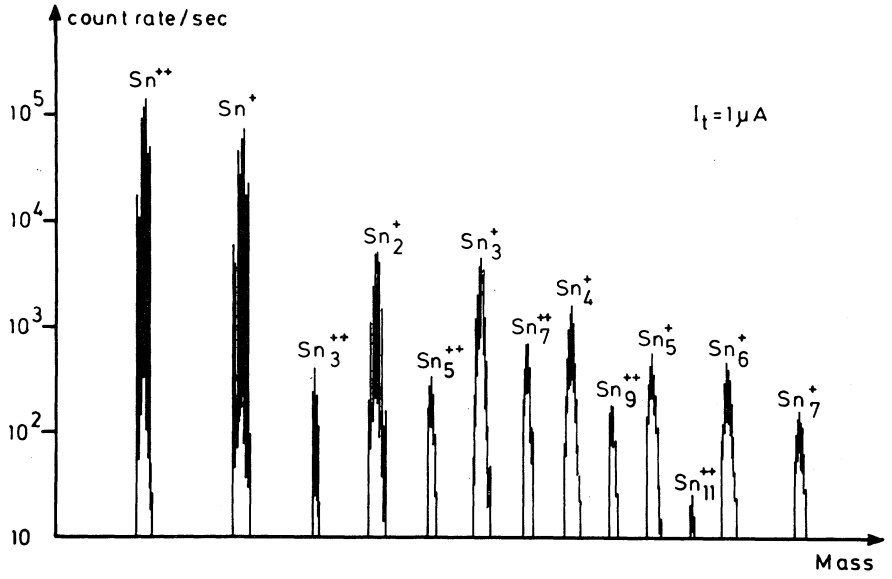


FIG. 1. Logarithmic intensity distribution of the main peaks in a mass spectrum of a liquid-metal field-ion source of tin. For the two main species $Sn^{++}$ and $Sn^{+}$, saturation effects in the Channeltron limit the count rate. These effects have been taken into account to provide the numbers in Table I.

TABLE I. Distribution, relative to $Sn^+$, of the peak heights for the most important identified masses. Note that the relative intensity of double-charge clusters is maximum for $n = 7$ in the low-current case but decreases regularly with $n$ at higher currents. The numbers are uncorrected for the unknown variation of detection efficiency for different masses.

| Species \ $I_t$ | 1 μA | 20 μA |
|---|---|---|
| $Sn^{++}$ | 2.1 | 3.2 |
| $Sn^+$ | 1 | 1 |
| $Sn_3^{++}$ | $1.9\times10^{-3}$ | $4.5\times10^{-4}$ |
| $Sn_2^+$ | $2.8\times10^{-2}$ | $2.6\times10^{-2}$ |
| $Sn_5^{++}$ | $1.9\times10^{-3}$ | $2.4\times10^{-4}$ |
| $Sn_3^+$ | $5.2\times10^{-2}$ | $1.3\times10^{-2}$ |
| $Sn_7^{++}$ | $3.9\times10^{-3}$ | $2.4\times10^{-4}$ |
| $Sn_4^+$ | $1.1\times10^{-2}$ | $3.9\times10^{-3}$ |
| $Sn_9^{++}$ | $1.1\times10^{-3}$ | ... |
| $Sn_5^+$ | $3.7\times10^{-3}$ | $1.3\times10^{-3}$ |
| $Sn_{11}^{++}$ | $2.1\times10^{-4}$ | ... |
| $Sn_6^+$ | $4.1\times10^{-3}$ | $1.1\times10^{-3}$ |
| $Sn_7^+$ | $7.9\times10^{-4}$ | $1.8\times10^{-4}$ |

In this expression $I_1$ is the first ionization potential of tin (7.3 eV), $\Lambda$ is the vaporization energy (~3.1 eV), and $\varphi$ is the work function (4.4 eV). We thus assume $\Delta V_c = 6$ V to define the absolute voltage scale in Fig. 2 because it has been checked that, at the lowest emission current, $\Delta V_c$ is the same for both the liquid and the frozen sources. This is strong evidence that the mechanism of emission is the same in the two cases confirming therefore the proposal by Gomer[15] that the field evaporation is the dominant mechanism at low total current. The position of the energy maximum, as a general trend, moves towards $V = 0$ as the current increases. One possible explanation is that direct field evaporation gives way to thermal evaporation followed by field ionization —in which case the term $\Lambda$ drops out of Eq. (1). Another possibility is that some of the ions are produced by field ionization in the vacuum, so that a free electron is accelerated to the tip with an energy of a few eV. It can bring Sn atoms in the surface to an excited state with a reduced effective $I_1$. These mechanisms have also been proposed by Kuk and Sakurai to explain the behavior of the intensity of the optical emission.[16]

The energy spectra show two main differences between $Sn^+$ and $Sn^{++}$ at a given current: Firstly, the distribution of $Sn^+$ is broader and secondly, it has a pronounced tail, even at the lowest emission current. The behavior of the half-width $\Delta V_{1/2}$ with current is shown in Fig. 3. Such differences

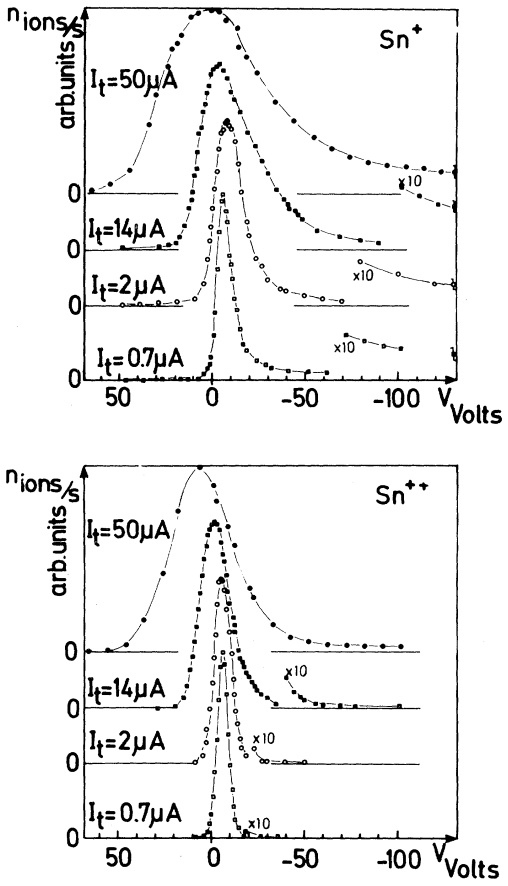


FIG. 2. Voltage distributions of $Sn^+$ and $Sn^{++}$ for different emitter currents measured with respect to the applied voltage (negative voltage corresponds to slower ions). Note that the $x$ scale is in volts and therefore the energy scale is equal to the voltage value multiplied by the charge of the ion. The $y$ scale is linear.

are similar to those observed for gold,[7] in which case one of the present authors had proposed an explanation in terms of resonant charge-transfer reactions between slow neutral and rapid ionized particles.[17] The relevant cross section is at least one order of magnitude smaller in the case of double-charge ions.

Generally, these results show the existence in the beam of ions possessing energy in excess of the applied voltage. This is evidence of Coulomb interactions in the beam after the production of ions. Following the theory developed by Knauer[18] for the Boersch effect in electron and ion beams, we can predict a dependence of $\Delta V_{1/2}$ as proportional to $I^{1/2}$ for given geometry of the emitting zone, which is not in contradiction with our data. However, since the important interactions are

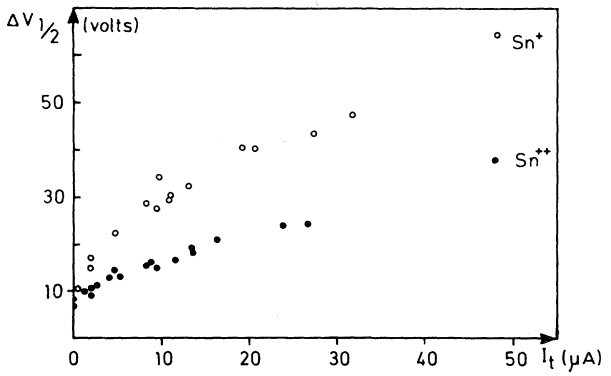


FIG. 3. Dependence of the full width at half maximum $\Delta V_{1/2}$ with total emitter current for $Sn^+$ and $Sn^{++}$.

between particles of the same velocity it is difficult to understand why the energy spread is of the same order of magnitude for different ion species, the intensity of which covers several orders of magnitude. We are consequently led to conclude that either the Boersch effect is so strong as to imply a complete redistribution of the initial thermal energy of the particles or that other processes are also occurring.

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